THE JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

JUNE 1, 1944

MONTHLY PUBLICATION DEVOTED TO THE ARTS AND SCIENCES RELATED TO THE SILICATE INDUSTRIES

TABLE OF CONTENTS

Vol. 27 June 1, 1944 No. 6

THE JOURNAL

Effect of Firing Atmosphere on Development of Colors in Ceramic Glazes 165–75

By William F. McDevit

Influence of Humidity on Dielectric Properties of High-Frequency Ceramics 175–81

By Henry H. Hausner

Calcination of Topaz Ore in a Rotary Kiln 181–85

By Gordon R. Pole

Calculation of Surface Tensions of Glasses 186–89

By Kenneth C. Lyon

Optical Glass from Viewpoint of Lens Designer 189–95

By R. Kingslake

Publication Office: 20th & Northampton Sts., Easton, Pa.
Editorial Office: 2525 N. High St., Columbus 2, Ohio
Committee on Publications: R. L. Stone, *Chairman;* R. E. Birch, H. Z. Schofield, H. Thiemecke, and R. C. Purdy, *ex officio*

Entered as second-class matter at the post office at Easton, Pa., under the act of March 3, 1879. Published monthly.
Subscription fifteen dollars ($15.00) a year. Single numbers $1.50
(Foreign and Canadian postage, 50¢ additional on subscriptions)
(Copyright 1944, American Ceramic Society, Inc.)

THE JOURNAL
OF
THE AMERICAN CERAMIC SOCIETY

Volume 27 June 1, 1944 Number 6

EFFECT OF FIRING ATMOSPHERE ON DEVELOPMENT OF COLORS IN CERAMIC GLAZES*

By William F. McDevit

Abstract

The effect of systematic variations in atmosphere between 100% oxidizing and 100% neutral was noted. The principles and definitions of color designation are given and possible physicochemical changes which result in color variation are considered. Experimental data indicate the relative stability of typical colors under atmospheric variations.

I. Introduction

A problem frequently encountered by the industrial ceramist is the maintenance of an acceptable degree of constancy in the color of glazed ceramic ware. One of the most important variables to consider is the composition of the furnace atmosphere.

The purpose of this research was to study the effect of this variable on the colors of several types of colored glazes. A number of specimens of each type was fired in controlled atmospheres of different compositions, and the resulting colors were measured. All other factors involved in the production of the glazes were held constant. A separate series of experiments in one case was carried out on the basic coloring oxides to correlate the effects observed in the glaze with a possible physicochemical mechanism for the development of the colors.

Five types of colored glazes were investigated. The same feldspathic base glaze was used in each case, and a stain derived from the oxides in the indicated system was added as follows: (1) Ca-Cr (light greens), (2) Va-Sn (yellow), (3) Fe-Cr-Zn (brown), (4) Cr-Sn (pink), and (5) Cr-Sn (maroon).

Cooke[1] studied the behavior of enamels as a function of atmosphere but was more interested in body-glass bonds than in color or quality. Watts[2] showed the effect of atmosphere on the quality of colorless low-temperature glazes. Peskin[3] presented data on the effect of furnace atmospheres on the color of pure Cr_2O_3, alone and when used as a pigment in a feldspathic glaze. With a few exceptions, other information relating to firing atmospheres and ceramic colors has been limited to incidental qualitative observations.

(1) Principles and Definitions in Color Designation

The three primary attributes of color, according to Judd,[4] are lightness, hue, and saturation. By "lightness" of a color is meant the location of the equivalent neutral or achromatic color in a scale ranging from black to white. "Hue" defines the spectral appearance of the color, that is, blue, green, yellow, red, purple, or whatever intermediate color it may match. "Saturation" is a measure of the purity of a color possessing hue, or in other words, its departure from neutrality or achromaticity. In terms of these three attributes, a color can be plotted in a solid figure in which lightness is measured along the vertical axis; hue, by the angular position around this axis; and saturation, by the perpendicular distance from the axis. Figure 1 shows a horizontal cross section (looking down) of such a solid. The axis of lightness is perpendicular to the paper, and, for neutral colors, passes through a central point, zero.

(2) Interpretation of Reflectometer Data

Specimens prepared in this investigation were measured on a Hunter reflectometer.* This instru-

---

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 4, 1944 (Design Division). Received October 27, 1943.

This investigation was carried out under an Edward Orton, Jr., Ceramic Foundation Fellowship at Rutgers University, New Brunswick, N. J.

[1] R. D. Cooke, "Effect of Furnace Atmosphere on Firing of Enamel," *Jour. Amer. Ceram. Soc.*, **7** [4] 277–81 (1924).

[2] A. P. Watts, "Effect of Furnace Atmospheres on Quality of Certain Types of Glazes," *ibid.*, **14** [6] 460–68 (1931).

[3] W. L. Peskin, "Effect of Furnace Atmosphere on Colors Derived from Chromic Oxide," *Bull. Amer. Ceram. Soc.*, **20** [11] 402–11 (1941).

[4] D. B. Judd and K. L. Kelly, "Method of Designating Colors," *Jour. Research Nat. Bur. Standards*, **23** [3] 355–85 (1939); R.P. 1239; *Ceram. Abs.*, **19** [4] 85 (1940).

* R. S. Hunter, Instructions for Use of Hunter Multipurpose Reflectometer. Unpublished.

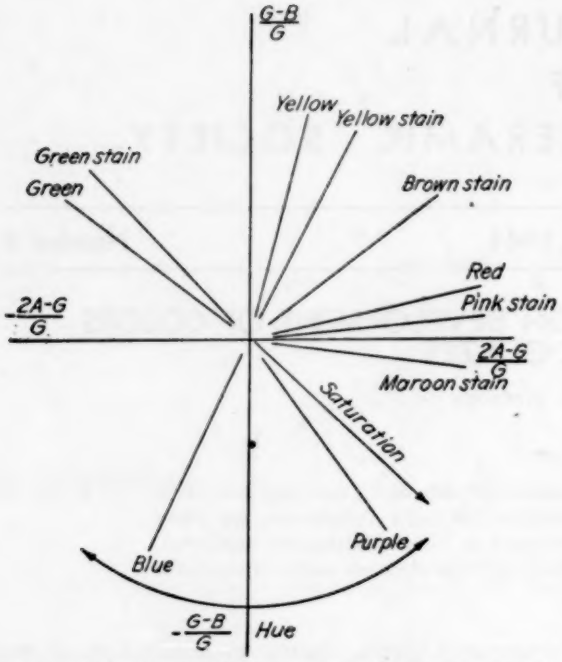

FIG. 1.—Color diagram for expressing reflectometer data in terms of hue and saturation.

ment makes use of the tristimulus method of measurement, giving values of percentage of reflectance for green, blue, and amber light. The color of the light is determined by corresponding filters located between the lamp and the reflecting surface. After passing through the filters, the light is split into two beams, one of which is reflected from the surface to be measured and allowed to fall on a movable photocell and the other is reflected from a standard surface onto a fixed photocell. The two photocells are connected to opposite poles of a galvanometer. In taking a reading, the movable photocell is moved along a rack normal to the unknown surface until the galvanometer indicates that the same amount of radiant energy is falling on the two photocells. Percentage of reflectance is read from a calibrated logarithmic scale. Because the incident beam strikes the unknown surface at an angle of 45 degrees, the (45°, 90°) reflectance may be measured. To correct for any changes which may take place in photocell response, lamp emission, or other factors, the instrument is adjusted from time to time with a surface of known reflectance values in place of the unknown surface. The adjustment is made by means of shims which change the angle of the standard reflecting surface so that the proper readings are obtained.

The lamp, filter, and photocell combination of this instrument is so chosen that the emission and response curves are similar to those of the I.C.I. standard illuminant and observer,[5] which makes it possible

[5] R. S. Hunter, "Multipurpose Photoelectric Reflectometer," *Jour. Research Nat. Bur. Standards*, **25** [5] 581–618 (1940); R.P. 1345; *Ceram. Abs.*, **20** [7] 175 (1941).

FIG. 2.—Apparatus for controlling compositions of atmospheres; O_2, oxygen tank; N_2, nitrogen tank; V, needle valves; R_1 and R_2, reservoirs; F_1 and F_2, flowmeters; T, mixing tube; D, drying tube ($CaCl_2$); C, Coors tube; E, furnace; L, thermocouple.

to employ the three values obtained on a diagram such as Fig. 1. The value along the coordinate of lightness, which is not shown on Fig. 1, is equal to the reading obtained through the green filter because this value is almost the true luminous reflectance for daylight illumination. Where A, G, and B represent the amber, green, and blue reflectances, respectively, plotting functions $\frac{G-B}{G}$ and $\frac{2(A-G)}{G}$ along the coordinate shown in Fig. 1 will locate the color of the specimen properly on that diagram. The reason for using G as the denominator is to give light and dark samples comparable ratings so that they may be plotted on the plane diagram.

Other functions to be employed in the interpretation of reflectometer data are $\frac{A-B}{G}$ as suggested by Hunter* for degree of yellowness and equation (1) as given by Balinkin[6] for the evaluation of small overall color differences.

$$E = 730(G^{1/2}(2\overline{\Delta a^2} + \overline{\Delta b^2} + (\overline{\Delta G^2})/300G)^{1/2} \quad \text{judds} \quad (1)$$

$$a = \frac{A-G}{3B+2A+5G}.$$

$$b = \frac{G-B}{3B+2A+5G}.$$

The judd is a unit of color difference developed by Judd[4] in terms of the I.C.I. trichromatic coefficients. It is defined in such a manner that the proper weight, in terms of visual perception, is given to values of hue, lightness, and saturation. In other words, all color differences of one judd appear to the eye to be of equal magnitude regardless of the location of the colors in the color solid and regardless of whether the difference is predominantly one of hue, lightness, or saturation.

II. Experimental Procedure

(1) Glazes and Lime-Chrome Mixture Preparation

A base feldspathic glaze of the following empirical composition was prepared by milling the proper mix-

[6] I. A. Balinkin, "Color Symposium: V, Measurement and Designation of Small Color Differences," *Bull. Amer. Ceram. Soc.*, **20** [11] 392–402 (1941).

ture of wet raw components for four hours, drying, and crushing:

$$\left.\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\} \quad 0.4\ Al_2O_3 \quad .\ 3.5\ SiO_2$$

Each of the five stains was mixed in the proper proportion with smaller batches of this glaze, and the mixtures were again milled to produce the five types of raw colored glazes investigated. Each glaze was applied by spraying on several white vitreous tile, $^3/_4$ by $1^1/_2$ in. in size. All tile to which a given glaze was to be applied were mounted together on a single base so that a uniform thickness of application could be maintained insofar as possible.

To show a relation between the effects of atmosphere on the color of the green glaze and its effect on the reaction obtained on calcination of CaO with Cr_2O_3, an intimate mixture of lime and chrome was prepared. This was done by wet milling a 1-to-1 mixture of $CaCO_3$ and Cr_2O_3 until a homogeneous mixture was obtained. This mixture was then dried and crushed before use.

(2) Apparatus for Atmosphere Control

The specimens thus prepared were treated individually in an electric resistance furnace, the heating chamber of which was a gas-tight muffle through which a mixture of gases could be streamed. The composition of this mixture and therefore of the atmosphere in which the glazes were fired could be controlled by fixing the rates of flow of the individual gases. Each specimen of a given glaze was thus fired in a different atmosphere of known composition. The firing atmospheres used ranged from neutral (100% nitrogen) to strongly oxidizing (100% oxygen). Most of the runs were made in atmospheres containing between 0 and 20% of oxygen because this is the most significant range in industrial production. Attempts to work with a reducing atmosphere using carbon monoxide resulted in the obscuring of the color effects by a number of factors, primary among which was the deposition of carbon. This aspect was therefore temporarily abandoned. In the experiments on lime-chrome mixtures, weighed samples were placed in a platinum boat and treated in the same manner. On completion of the run, these samples were removed and weighed before being prepared for color measurement.

The arrangement of the apparatus was similar to that used by Peskin[3] (Fig. 2). The gases used were c.p., and the atmosphere composition was determined by the ratio of the rates of flow of the nitrogen and oxygen, as measured by the flowmeters, F_1 and F_2, into the mixing tube, T. In making a run, the desired rates of flow were adjusted at the start, the total rate being 10 cc. per second, and the flow was allowed to continue for one-half hour after the heating current had been shut off. The same atmosphere composition was maintained throughout the heating schedule. This is a condition which of course is not analogous to commercial conditions but which is necessary for significant interpretation of the results.

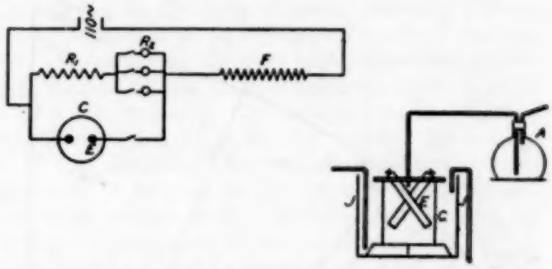

FIG. 3.—Electrolytic arrangement for maintaining constant heating schedules; R_1, rheostat; R_2, heating coil resistances; F, furnace winding; C, cell; E, carbon electrodes; J, water jacket; A, reservoir.

The electrical furnace was platinum wound. It was cylindrical in shape, 12 in. long and 10 in. in diameter. A gas-tight Coors tube, C, 24 in. long and $1^1/_4$ in. in inside diameter, passed through the center and served as a heating chamber. The platinum wire (20-gauge) was wound around this tube over a length of 11 in. in the middle. The insulation in the furnace consisted of a layer of light calcined magnesia and a layer of insulating cement.

(3) Apparatus for Constant Heating Schedules

Because one of the factors involved in the production of a colored glaze is the nature of the thermal treatment, the heating cycle was kept uniform and constant from run to run. The setup which was used to enable the automatic duplication of heating curves is diagramed in Fig. 3. The principle is simply that the resistance of an electrolytic cell for a given solution concentration is inversely proportional to the area of contact between the electrodes and the solution and directly proportional to the distance apart of the electrodes. If the relative positions of the electrodes remain fixed, the resistance of the cell depends on the level of the solution in the cell. In practice, a certain amount of solution (300 cc.) was placed in the cell (C) so that the level was just below the tips of the carbon electrodes (E); 700 cc. of the solution were placed in the reservoir and, at the beginning of the run, were allowed to start dripping into the cell through a siphon arrangement. At the same time, the full-line voltage was put across the circuit. From then on, the cell resistance decreased at a rate depending on the rate at which the solution level rose.

The heating rate of the furnace depended, of course, on the power input and any variation which might take place in it. The power consumed by the furnace at the beginning of a run was low because its resistance was low and that of the external circuit (see Fig. 3), which was determined by the resistance of the cell, was high. The external resistance was lowered by the rise in level of the solution in the electrolytic cell; the power consumed by the furnace rose, and its temperature increased accordingly. The factors, such as resistance (R_2), solution concentration and its rate of flow, and size and position of the electrodes, were chosen so that a desirable heating cycle

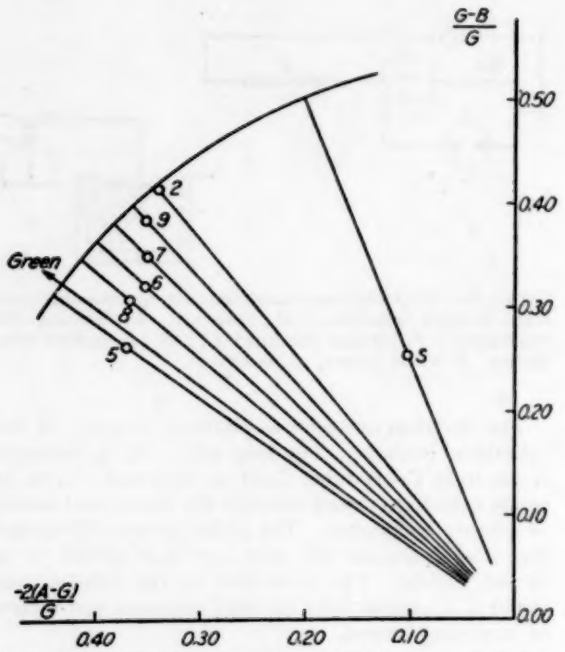

FIG. 4.—Colors of green glazes fired in various atmospheres.

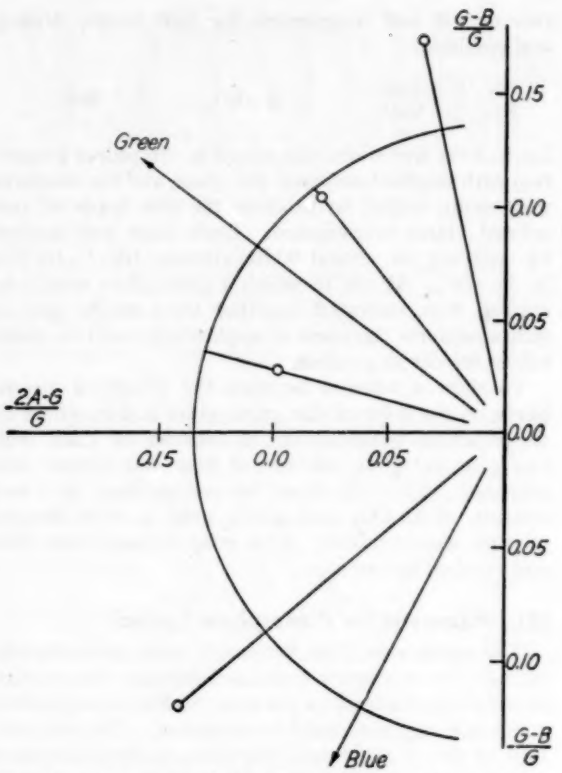

FIG. 5.—Colors of samples of lime-chrome mixture calcined in various atmospheres.

resulted. This cycle was 3 hours long; 2¼ hours were taken to reach the maturing temperature of 1260° to 1265°C., and the final soaking period was ¼ hour. It was necessary to cool the cell with a water jacket to eliminate the effect of temperature on its resistance. Heating curves for runs in which this device was used checked with one another to within 5°C.

(4) Color Measurement

The glazed surfaces of the specimens, which were measured on the Hunter reflectometer, presented an area of 1½ by ¾ in. The opening in the instrument over which the specimen surface was placed needed an area of about 2 by 3 in. A special window was therefore prepared to fit over this opening for measuring the smaller specimens. A rectangular opening for this purpose was cut in a piece of heavy unglazed black paper; the area of this opening was slightly less than that of the specimens, and the total area of the paper (including the opening) was large enough to cover the opening in the reflectometer. The window was fitted over a frame, which was made so that the specimen could be accurately positioned. When measurements were made, this frame was placed so that the window opening was always at exactly the same location within the reflectometer opening, near its center.

This decrease in area presented for measurement would be expected to result in a corresponding decrease in reflectance readings below what they normally would be. To compensate for this, a window of exactly the same nature was used in standardizing the instrument with a surface of known reflectance values.

Because the instrument is most accurate for the higher ranges of reflectances, there was a slight decrease in accuracy arising from the use of smaller areas. The reflectance values of the measured specimens, in terms of the usual method of measurement, nevertheless remained well within the range for which the instrument was designed. The color attribute for which the greatest possible error must be admitted is that of saturation because the small amount of light which is reflected from the black surface surrounding the window opening could have had a dilution effect. Even in this respect, however, color values differing over only a small range may be taken as comparable. Reflectance readings made in this manner were reproducible to within 0.5% and may be considered valid for purposes of measuring small color differences. No claim is made for the degree of accuracy in terms of absolute color specification.

The manner of preparing the samples of the lime-chrome mixture for measurement is similar to that suggested by Merwin[7] and used by Peskin[3] in his work with Cr_2O_3. The samples were first ground in an agate mortar until they passed through 325 mesh. One gram of each sample was thoroughly mixed on a glass plate with 5 gm. of zinc oxide (Green Seal) and 5 cc. of c.p. glycerin. The resultant paste was then spread on a 3- by 4-in. glass slide and covered with a colorless cover glass. The reason for the use of the zinc oxide was to raise the reflectance values so they

[7] H. E. Merwin, "Optical Properties and Theory of Color of Pigments and Paints," *Proc. Amer. Soc. Testing Materials*, **17**, 494 (1917).

would not fall below the sensitive range of the instrument. The glass plates were held together and in the proper place by spring clips. For purposes of comparison, a measurement of the stain used in the green glaze was made in this manner.

III. Light Green Glazes

The stain mixture was pulverized wet, calcined at 1260°C., ground, and levigated; it was then added to the base feldspathic glaze to the extent of 15% by weight.

Composition of stain	Parts by weight
SiO_2	12.5
$CaCO_3$	10.0
Kaolin	4.25
$K_2Cr_2O_7$	10.0
Pb_3O_4	3.75
$CaSO_4 \cdot 2H_2O$	3.0

(1) Review of Literature

The essential oxides in the production of a light green stain are those of calcium and chromium.[8] Chromium oxide (Cr_2O_3) alone produces a dark green color. The presence of CaO in the stain has a diluting or lightening effect, but no reference to the exact mechanism has been found.

The only stable oxide of chromium above 550°C. is Cr_2O_3. Below this temperature, a number of nonstoichiometric oxides intermediate between CrO_3 and Cr_2O_3 have been listed,[9] the higher oxides being stable at the lower temperatures. Milbauer[10] and Blanc and Chaudron[11] mention the possible conversion of Cr_2O_3 to a higher oxide under high oxygen pressure. Peskin[3] observed that green Cr_2O_3 undergoes a color change toward blue when heated above 1000°C. and that the magnitude of this change increased with an increase of the oxygen content of the furnace atmosphere. He attributed this change to the formation of a higher oxide of chromium at the surface of the particles at the higher temperatures. This higher oxide then vaporized, was redeposited on other chrome particles, and eventually decomposed to form the original compound, Cr_2O_3. The change in color was attributed to the resultant change in surface structure of the Cr_2O_3 particles.

When CaO and Cr_2O_3 are heated together, a reaction occurs. According to Vasenin,[12] calcium chromite ($CaO \cdot Cr_2O_3$) in the form of green prismatic crystals is formed at 1020°C. and above. He stated that calcium chromate was the first substance which tended to be formed at 600°C. and decomposed at 1020°C. to form the chromite. On the other hand, Nargund and Watson[13] and Athavale and Jatkar[14] list a number of compounds in a higher state of oxidation which are stable in various ranges at high temperatures. The latter authors give a series of reactions in the thermal decomposition of calcium chromate ($CaCrO_4$), which indicate those compounds and their ranges of stability.

$$24CaCrO_4$$
$$860° \downarrow\uparrow$$
$$3(8CaO \cdot 4CrO_3 \cdot 2Cr_2O_3)$$
$$915° \downarrow\uparrow$$
$$8(3CaO \cdot CrO_3 \cdot Cr_2O_3)$$
$$1030° \downarrow\uparrow$$
$$3(8CaO \cdot 2CrO_3 \cdot 3Cr_2O_3)$$
$$1125° \downarrow\uparrow$$
$$x(5CaO \cdot CrO_3 \cdot 2Cr_2O_3)$$
$$1265° \downarrow\uparrow$$
$$12CaO \cdot 12(CaO \cdot Cr_2O_3)$$

These reactions were studied at low pressures so that the stability ranges under conditions of atmospheric pressure would be somewhat different, probably higher.

(2) Experimental Results

The reflectance measurements for specimens of the green glaze fired in various atmospheres are given in Table I with the necessary values for the functions, $\frac{2(A-G)}{G}$ and $\frac{G-B}{G}$, for locating the colors on the diagram in Fig. 1. Figure 4 is an enlargement of the second quadrant of this diagram and shows the location of the colors of the specimens.

Table I also gives the reflectance measurements on the samples of the CaO-Cr_2O_3 mixture treated in various atmospheres. The color values are plotted in Fig. 5. The percentage of weight increases are corrected for loss of CO_2 from calcium carbonate.

(A) Changes in Hue: Visual examination of the glazes showed a consistent change in hue from blue-green toward yellow-green with increasing oxygen content in the firing atmosphere. An analogous change of greater magnitude could be readily observed in the CaO-Cr_2O_3 mixtures.

Figures 4 and 5 show these hue changes graphically in terms of the angular change in the radii drawn from the neutral point through the points representing the colors. The hue values of the green glazes shift from the blue side of green past true green toward yellow; in the CaO-Cr_2O_3 mixture, the change is from a greenish blue through true green toward yellow. The amounts of the changes as a function of atmos-

[8] A. R. Heubach, "Light Green Chromium Stains," *Trans. Amer. Ceram. Soc.*, **14**, 418–33 (1912).

[9] (*a*) A. Cameron, E. H. Harbard, and A. King, "Nonstoichiometric Oxides: I, Oxides of Chromium," *Jour. Chem. Soc.* [London], **1939**, pp. 55–61.

(*b*) S. S. Bhatanager, A. Cameron, E. H. Harbard, P. L. Kapur, A. King, and Brahm Prakash, "Magnetic Susceptibilities of Metallic Oxides with Special Reference to Those of Chromium and Manganese," *ibid.*, **1939**, 1433–41; *Ceram. Abs.*, **20** [4] 104 (1941).

[10] J. Milbauer, "Action of Oxygen on Metallic Oxides at High Temperature and Pressure," *Chem. Ztg.*, **40**, 587 (1916); *Chem. Abs.*, **10** [20] 2558 (1916).

[11] L. Blanc and G. Chaudron, "Transformations and Oxidation of Sesquioxides of Chromium," *Compt. rend.*, **182** [1] 386–88 (1926).

[12] F. I. Vasenin, "Reciprocal Action of CaO and Cr_2O_3 on Heating, I," *Vsesoyuz. Nauch.-Issledovatel. Inst. Tsement.*, No. 17, pp. 40–51 (1937); *Ceram. Abs.*, **17** [8] 291 (1938).

[13] K. S. Nargund and H. E. Watson, "Reactions of Chromates at High Temperatures: II, System Lime-Chromium Oxide–Oxygen," *Jour. Indian Inst. Sci.*, **9A**, 149–67 (1926); *Ceram. Abs.*, **6** [10] 475 (1927).

[14] V. T. Athavale and S. K. K. Jatkar, "Reactions of Chromates at High Temperatures: III, Decomposition of Calcium Chromate," *Jour. Indian Inst. Sci.*, **20A** [8] 55–66 (1937); *Ceram. Abs.*, **19** [1] 30 (1940).

TABLE I

REFLECTANCE MEASUREMENTS FOR GREEN GLAZE AND $CaO\text{-}Cr_2O_3$ SPECIMENS FIRED IN VARIOUS ATMOSPHERES

Composition of atmosphere (%)		Run No.	Reflectances			$\frac{2(A-G)}{G}$	$\frac{G-B}{G}$	$\frac{A-B}{G}$
O_2	N_2		Green	Amber	Blue			
			Green glaze specimens					
0	100	5	0.408	0.333	0.301	−0.368	0.262	0.0785
5	95	8	.404	.330	.280	.366	.307	.0990
10	90	6	.381	.314	.259	.352	.320	.1445
20	80	7	.377	.311	.245	.350	.350	.1751
50	50	9	.371	.228	.306	.385	.350	.2101
100	0	2	.352	.292	.206	.341	.415	.2423
Stain		S	.660	.633	.528	.103	.254	
			$CaO\text{-}Cr_2O_3$ specimens					Weight increase (%)
0	100	101	0.424	0.394	0.475	−0.1419	−0.1205	1.71
20	80	102	.486	.462	.473	.0987	+0.0267	5.04
50	50	103	.500	.480	.448	.0800	+0.1041	5.95
100	0	104	.499	.490	.413	.0360	+0.1722	6.22

phere composition are more clearly shown in Fig. 6. These curves were determined by construction in the manner suggested by Peskin.[3] A circle of arbitrary radius was drawn through the color points. Hue comparisons can thus be made at equal saturation. The intersection of the radius which indicates the hue "true green" was used as a reference point. The distances between this point and those determined by the intersections of the other radii and the circle were taken from the diagram with dividers and plotted on Fig. 6 as ordinates against percentage of oxygen in the furnace atmosphere as abscissae. In the $CaO\text{-}Cr_2O_3$ mixture, the scale units of the color diagram (Fig. 5) were doubled for convenience of the plot and the radius of the reference circle was halved in order to make the hue changes comparable with those of the glazes.

Figure 6 shows that the change in hue of the glazes is greatest for the first increment of oxygen. The slope of the curve shows that the hue changes become successively smaller as the oxygen content is increased. The most critical atmosphere compositions are those between 0 and 20% of oxygen, which corresponds to the range of commercial firing atmospheres.

The slope of the curve for the $CaO\text{-}Cr_2O_3$ mixtures varies in a similar manner, though not so markedly. This bears out the analogy between the two cases to be discussed later.

(*B*) *Degree of Yellowness:* That the change in hue of the glazes is essentially one of increasing yellowness with increasing oxygen content of the firing atmosphere is shown in Fig. 7, where degree of yellowness, $\frac{A-B}{G}$, is plotted against percentage of oxygen. Here again, the slope is greatest in the range of lower oxygen content.

(*C*) *Change in Lightness:* The variation of the color attribute, lightness, with the composition of the firing atmosphere is shown for the green glazes in Fig. 8, where *G* is plotted against atmosphere composition. The first 20% of oxygen again is the critical range, where the greatest variations can take place.

(*D*) *Discussion of Over-All Color Change of Glazes:* In order that their magnitude might be more easily

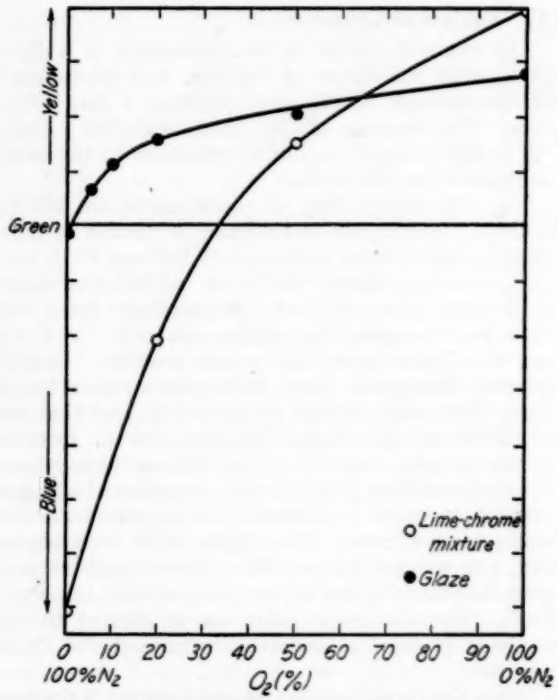

FIG. 6.—Hue change vs. composition of firing atmosphere for green glaze and lime-chrome mixture.

understood in terms of visual perception and commercial tolerances, the over-all color differences among the glazes fired in the critical range of 0 to 20% of oxygen have been calculated in judds.

According to Balinkin,[6] 0.2 judd is the smallest color difference perceptible to the eye; 2.5 judds is given as the maximum acceptable variation that an observer will accept for colored articles which are supposed to be uniform, such as in wall tile.

From these data, it can be concluded that variations of more than 10% in the atmosphere in which this glaze is fired can cause variations in color which are unacceptable. Within the range of 10 to 20% of O_2, variations in atmosphere composition will not be likely to

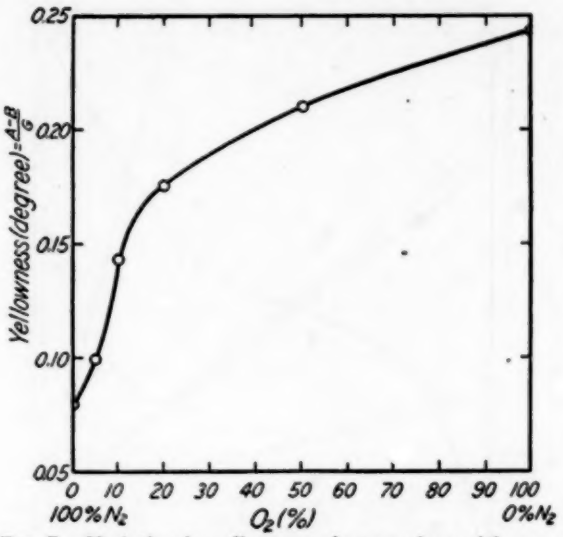

FIG. 7.—Variation in yellowness of green glaze with composition of firing atmosphere.

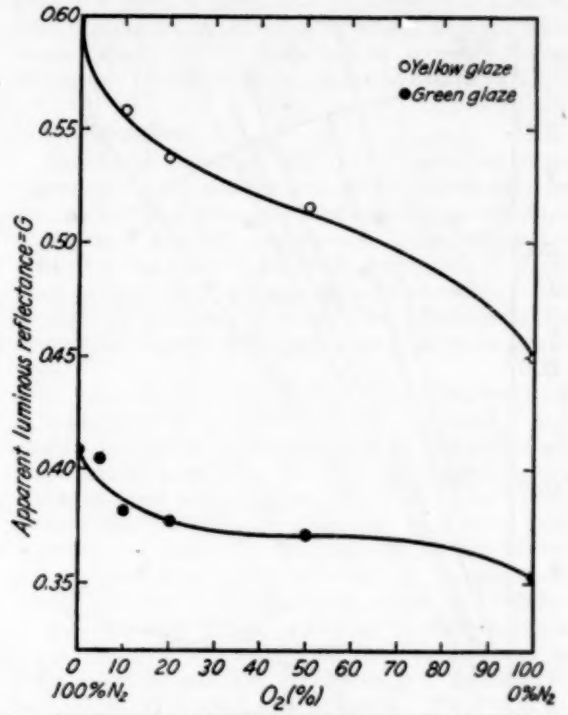

FIG. 8.—Variation of lightness with composition of firing atmosphere.

cause unacceptable color differences. If the atmosphere contains less than 10% of oxygen, a variation of 5% or less in its composition may cause corresponding color differences which are unacceptable. Preparation of samples on which more accurate measurements can be made is necessary before these limits can be more strictly defined.

TABLE II

$$E \text{ (judds)} = 730(G^{1/2}(2\overline{\Delta a}^2 + \overline{\Delta b}^2 + (\overline{\Delta G}^2)/300G)^{1/2}$$

Firing atmosphere variation (%)	Judds
0–20	6.4
0–5	3.2
5–10	2.1
10–20	2.4

(3) Possible Physicochemical Nature of Changes

From a consideration of the data presented here as well as the information gained from the literature, a number of significant facts can be stated.

(1) The color changes in the glaze and in the CaO-Cr_2O_3 mixture seem to be analogous. The changes in the glaze were less marked, but this effect is expected because, in the preparation of the stain, a protective glass coating is formed around the pigment particles by the fusion of the auxiliary components. The tendency of this coating is to inhibit or arrest interaction between the pigment and atmosphere. In the commercial production of stains, this glass formation is usually encouraged in order to increase their stability.

(2) Calcium oxide and the oxides of chromium react chemically at high temperatures as has been brought out fairly conclusively in the literature. Visual examination of the samples of the lime-chrome mixtures treated in this research showed unmistakable indications of reaction, particularly in the case of the samples treated in pure oxygen where well-formed needlelike crystals had been developed.

(3) The products of this reaction may be in varying states of oxidation depending on the conditions, primarily temperature and atmosphere, under which the reaction has taken place. The work of Nargund and Watson[13] and of Athavale and Jatkar[14] gives the best evidence for this effect. It might be expected, then, that the state of oxidation will increase with the partial pressure of oxygen in the atmosphere. The weight increases observed in the mixtures studied in this investigation give qualitative support for this increase because they are a function of the oxygen content of the atmosphere.

(4) If the last point is granted, then the color observations on the samples show that the tendency toward increased state of oxidation of the calcium-chrome complex is accompanied by a tendency for its color to change from blue-green toward yellow and vice versa. This seems logical because the color of the least oxidized end point, calcium chromite, is described as "dark green" and that of the other end point, calcium chromate, as yellow.

(5) The color of the stain from which the raw glazes were prepared was yellow-green and considerably more yellow than any of the fired glazes.

From these considerations, a possible mechanism for the color variations can be described. The stain was calcined in an oxidizing atmosphere. The first important reaction to take place was the decomposition of $K_2Cr_2O_7$ at 500°C. The resulting chromic oxide reacted with the lime to form the calcium-chrome complex stable at this temperature. As the temperature was raised, this complex became unstable and

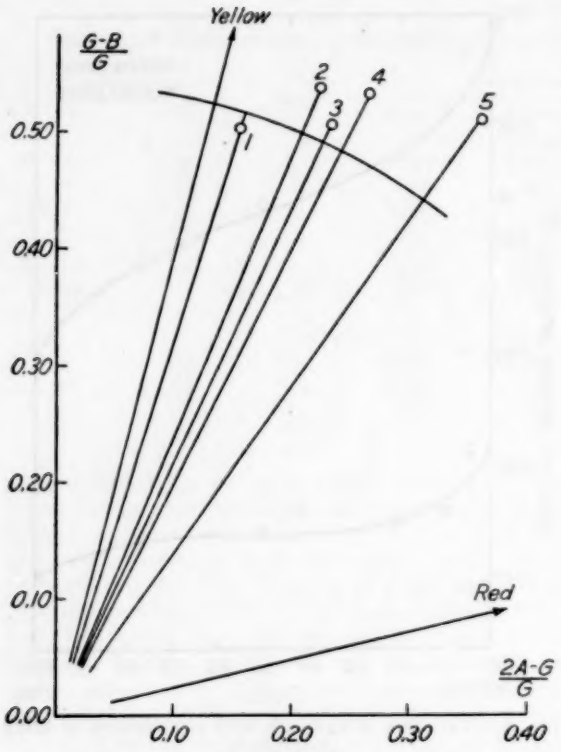

FIG. 9.—Colors of yellow glazes fired in various atmospheres.

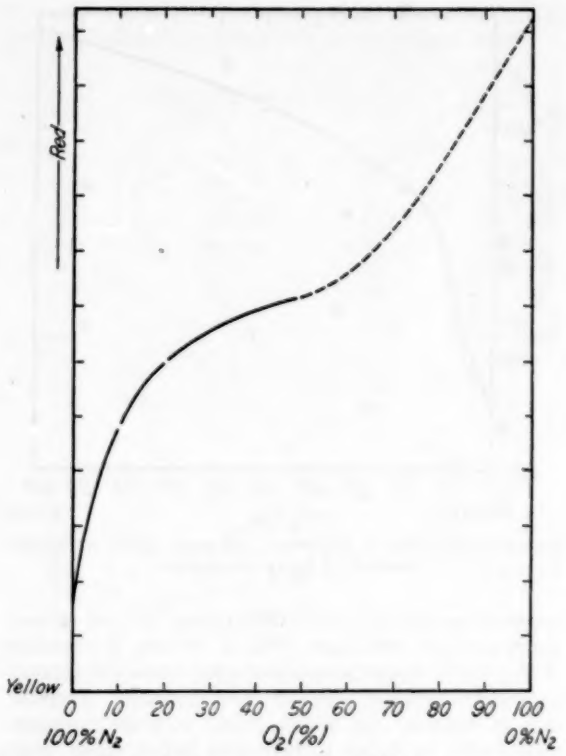

FIG. 10.—Hue change vs. composition of firing atmosphere for yellow glaze.

TABLE III

REFLECTANCE MEASUREMENTS OF YELLOW GLAZES FIRED IN VARIOUS ATMOSPHERES

Composition of atmosphere (%)		Run No.	Reflectances			$\frac{2(A-G)}{G}$	$\frac{G-B}{G}$
O_2	N_2		Green	Amber	Blue		
0	100	1	0.600	0.646	0.299	0.153	0.501
10	90	2	.558	.619	.258	.222	.537
20	80	3	.538	.600	.266	.232	.506
50	50	4	.514	.582	.240	.265	.533
100	0	5	.450	.531	.220	.360	.511

tended to decompose into a less oxidized form. The rate of this reaction was arrested when glass formation started. The less oxidized complex, stable at that temperature, was therefore not formed before the heat-treatment was ended. When glazes containing this stain were fired, the decomposition of the complex toward the more stable form continued, although at a slow rate because of the inhibiting effect of the protective glass coating. A corresponding change in color away from yellow attended this trend. The lower the oxygen content of the atmosphere, the lower was the state of oxidation of the stable complex toward which this change was directed. Likewise, from the law of mass action, the rate of this change toward a lower state of oxidation increased as the partial pressure of oxygen in the atmosphere decreased. Therefore, as the oxygen content of the firing atmosphere was decreased, lower states of oxidation of the pigmentary calcium-chrome complex were attained, and the colors of the glazes underwent correspondingly greater changes away from the yellow-green of the original stain toward a blue-green.

IV. Yellow Glazes

The composition of the yellow stain was SnO_2 96.0 and NH_4VO_3 4.0 parts by weight.

This mixture was calcined at 1260°C., ground, and levigated. It was then added to the base feldspathic glaze to the extent of 12% by weight.

There is little available information on the properties and constitution of vanadium-tin colors. Vanadium forms at least five oxides: V_2O, V_2O_3, V_3O_3, V_2O_4, and V_2O_5. The latter three are very stable and their reduction, even at high temperatures, requires a strong reducing agent, such as hydrogen or carbon monoxide. Vanadium oxide (V_2O) and V_2O_3 are easily oxidized and readily soluble in dilute acid. Black V_2O_3 is relatively insoluble but tends to oxidize to blue V_2O_4 on standing in air; V_2O_5 is orange-red in color and slightly soluble in water, forming a yellow solution.

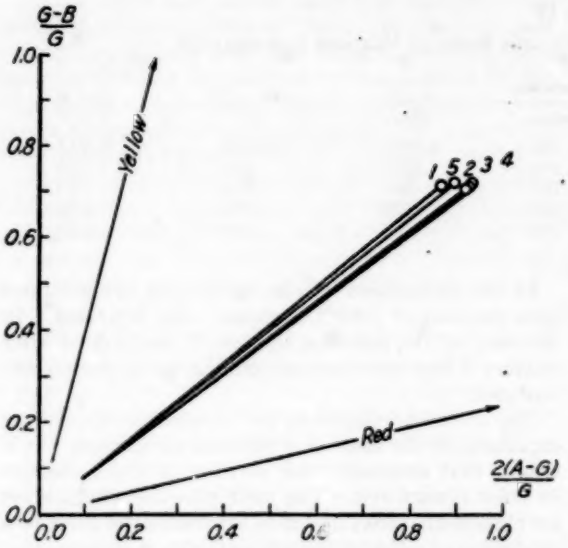

FIG. 11.—Colors of brown glazes fired in various atmospheres.

(1) Experimental Results

The reflectance measurements for specimens of the yellow glaze fired in various atmospheres are given in Table III with the values of the functions necessary for plotting the colors on the color diagram. This plot is made on Fig. 9, which is an enlargement of the first quadrant of Fig. 1.

(*A*) *Changes in Hue:* Visual examination of the glazes showed a variation in hue ranging from a light yellow for the specimen fired in a neutral atmosphere to a mottled orange-yellow for specimens fired in pure oxygen. The angular changes in the radii drawn through the color points show this change to be consistent from yellow toward red with increasing percentage of oxygen in the firing atmosphere. These hue changes are plotted against atmosphere composition in Fig. 10. This plot was made by construction in the manner described for the green glazes.

Figure 10 shows that the greatest change in hue again occurs with the first increment of oxygen in a neutral atmosphere. The slope of the curve drops off as 50% of oxygen is approached in a manner similar to that of the green glazes. Between 50 and 100% of oxygen, an anomalous rise in rate of change occurs. Further investigation of this portion of the curve will be necessary before its exact shape can be determined, but it is of little practical significance because it lies well beyond the range of commercial firing atmospheres.

(*B*) *Change in Lightness:* Values of *G* are plotted against atmosphere composition in Fig. 8. The similarity between this curve and the one for the green glaze is shown. The greatest variation in this attribute again takes place in the range from 0 to 20% of oxygen.

(*C*) *Over-All Color Change:* The over-all color difference between the specimen fired in 100% of nitrogen and the one fired in 20% of oxygen was calculated to be 6.3 judds, which is considerably greater than the visually acceptable variation of 2.5 judds. The preparation of samples on which more accurate measurements can be made will be necessary before the range of tolerable variation can be established.

(2) Discussion

Because of the small amount of vanadium oxide necessary for the development of the yellow color, its pigmentary properties can be explained on the basis of a purely physical phenomenon. This explanation attributes the color to a colloidal deposition of vanadium oxide on the inert stannic oxide particles. The mechanism has been demonstrated conclusively for chrome-tin pinks, and the two cases seem to be analogous.

On this basis, no ready explanation for the variation in color with firing atmosphere presents itself. Any change in the state of oxidation of the vanadium is unlikely because V_2O_5, the only yellow oxide, is very stable at these temperatures. No intermediate compounds between V_2O_4 or V_2O_3 and V_2O_5 have been reported. A change in the physical nature of the colloidal deposition seems more likely. Another possibility may be a variation in the degree of solubility of the vanadium oxide, analogous to what happens when orange-colored solid V_2O_5 dissolves in water to form a yellow solution. Andrews and Zwermann[15] mention in their work the possibility of solution in vanadium yellow enamel colors.

V. Brown Glazes

The composition of the brown stain was $K_2Cr_2O_7$ 2.0, SiO_2 2.0, ZnO 4.0, and FeO 1.0 parts by weight. The stain was produced by calcination of this mixture at 1260°C., followed by crushing and levigation, and it was added to the extent of 10% of the base feldspathic glaze.

Zinc oxide reacts with chromate salts to form a stable zinc chromate. The formation in artificial melts of a spinel, zinc ferrate, has been reported.[16] X-ray studies on the system Fe_2O_3–Cr_2O_3 showed that these rhombohedral compounds form a continuous series of solid solutions.[17]

The effect of atmosphere composition in the calcination of pure iron oxide is marked. The state of oxidation of iron oxide at high temperatures is dependent on the partial pressure of oxygen in the atmosphere with which it is in equilibrium. Studies of the equilibrium relationships of Fe_2O_3, Fe_3O_4, and oxygen[18]

[15] A. I. Andrews and C. H. Zwermann, "Fundamentals of Colors in Porcelain Enamels," *Jour. Amer. Ceram. Soc.*, **22** [3] 65–72 (1939).

[16] (*a*) E. Posnjak, "Crystal Structures of Magnesium, Zinc, and Cadmium Ferrites," *Amer. Jour. Sci.*, **19**, 67–70 (1930).

(*b*) H. E. Merwin, "System MgO–FeO–Fe_2O_3 in Air at One Atmosphere," *ibid.*, **21**, 145–57 (1931); *Ceram. Abs.*, **11** [3] 202 (1932).

[17] P. E. Wretblad, "X-Ray Studies on Systems Fe_2O_3–Cr_2O_3 and Fe_2O_3–Mn_2O_3," *Z. anorg. allgem. Chem.*, **189** [4] 329–36 (1930); *Ceram. Abs.*, **9** [10] 881 (1930).

[18] J. W. Greig, E. Posnjak, H. E. Merwin, and R. B. Sosman, "Equilibrium Relationships of Fe_3O_4, Fe_2O_3, and Oxygen," *Amer. Jour. Sci.*, **30** [5] 239–316 (1935); *Ceram. Abs.*, **15** [2] 74 (1936).

TABLE IV

REFLECTANCE MEASUREMENTS OF BROWN GLAZES FIRED IN VARIOUS ATMOSPHERES

Composition of atmosphere (%)		Run	Reflectances			$\frac{2(A-G)}{G}$	$\frac{G-B}{G}$
O_2	N_2	No.	Green	Amber	Blue		
0	100	1	0.130	0.186	0.037	0.862	0.715
5	95	2	.130	.190	.037	.922	.715
10	90	3	.128	.187	.036	.922	.718
50	50	4	.131	.191	.038	.916	.710
100	0	5	.124	.179	.034	.885	.725

have shown that Fe_2O_3 undergoes considerable decomposition to black Fe_3O_4 at temperatures above 1150°C. in the absence of oxygen. This decomposition does not take place in air until temperatures above 1380°C. are reached. At these temperatures, reducing atmospheres will lower the state of oxidation of the iron to the ferrous state.

According to Minton[19] and Pillai,[20] the formation of yellow-brown zinc chromate and yellow-brown Fe_2O_3 is the basis of the brown colors derived from the iron–chrome–zinc system.

(1) Experimental Results and Color Changes

Table IV gives the reflectance measurements on the specimens of brown glaze. The colors plotted in terms of the $\frac{G-B}{G}$ and $\frac{2(A-G)}{G}$ values are shown in Fig. 11.

Visual examination of the specimens yielded no perceptible variations in color. Figure 11 shows this constancy. The reflectance values for this set of specimens are considerably lower than in the previous cases and occur within the least accurate range of the instrument. Therefore, the variations indicated may be considered to be the result of experimental error.

The constancy of the colors produced indicates the stability of the pigmentary substances. The existence of zinc chromate and free Fe_2O_3 as pigmentary agents in the final glaze is therefore highly questionable. Zinc chromate, heated over a Bunsen burner, undergoes a series of permanent changes in color from yellow-brown to black. The firing temperature was also just in the range in which the atmosphere composition is most critical in determining the state of oxidation of the iron.

The literature has shown that Cr_2O_3 and Fe_2O_3 are isomorphous and that the formation of a $ZnO \cdot Fe_2O_3$ spinel takes place in artificial melts. In view of its indicated stability, it is very possible that the mineral formed in the present case is a similar spinel in which part of the iron is replaced by Cr_2O_3.

VI. Pink and Maroon Glazes

The pink and maroon stain compositions used are shown in the opposite column.

In the production of the stains, the raw mixtures were calcined at 1260°C., ground, and levigated. In the case of the maroons, mixture B was added after mixture A had been calcined and the whole process was repeated.

The colors developed in the chrome–tin system are explained on the basis of a physical mechanism. It is known that extremely fine division of Cr_2O_3 changes its color toward red. The most plausible explanation for chrome-tin pinks and reds attributes the color to a deposition of colloidal chrome on the inert stannic oxide particles.[21] The concentration of the colloidal layer probably determines the shade.

Most of the factors involved in the development of the colors are understood only in an empirical sense. It is known, for example, that increase of lime content in the glaze or stain changes the resulting color toward lilac.[21] A reducing atmosphere produces a scumming effect on chrome-tin glazes, which is attributed by Mellor[22] to the reduction of stannic oxide to the stannous form followed by its solution in the glaze. When oxidizing conditions are restored on the cooling cycle, the stannous oxide on or near the surface is oxidized to the less soluble, white stannic form. Because this precipitate is not covered by the colloidal chrome, it appears as a white scum on the surface.

(1) Experimental Results and Color Changes

The results obtained on firing specimens in various atmospheres were analogous for these two glazes. Accurate reflectance measurements could not be made for the maroon glaze on account of the extremely low reflectance values. Because of improper body-glaze fit characteristics, the surfaces of the specimens of pink glaze prepared thus far have been too uneven for other than visual examination.

Specimens of both types of glaze were fired in atmospheres containing 0, 5, 10, 20, 50, and 100% of oxygen.

Pink (parts by wt.)		Maroon (parts by wt.	A	B
SnO_2	10.0	$K_2Cr_2O_7$	4.5	1.2
$CaCO_3$	4.0	$Pb(C_2H_3O_2)$	12.0	1.5
SiO_2	4.0	SiO_2	58.0	
CaF_2	1.5	$CaCO_3$	80.0	
$PbCrO_4$		SnO_2	110.0	
		KNO_3	3.5	

[19] R. H. Minton, "Influence of Some Unusual Zinc Compounds in a Chrome Green Glaze," *Trans. Amer. Ceram. Soc.*, **17**, 667–71 (1915).

[20] D. S. Pillai, "Effect of Zinc Oxide on Coloring Properties of Chromium, Cobalt, and Iron Oxides," *Trans. Ceram. Soc.* [England], **25** [3] 209–19 (1925–1926); *Ceram. Abs.*, **6** [3] 91 (1927).

[21] R. C. Purdy and G. H. Brown, "Study of Chromium Tin Pinks," *Trans. Amer. Ceram. Soc.*, **11**, 228–61 (1909).

[22] J. W. Mellor, discussion of "Notes on Chromium Red Glaze," by C. E. Ramsden, *Trans. Ceram. Soc.* [England], **11**, 29–37 (1912); p. 36.

Visual inspection showed that the essential color variation is one of lightness. Glazes fired in the more neutral atmospheres were noticeably lighter than those fired in oxidizing atmospheres. Examination of the cross sections of the glazes showed the lightness to be only a surface phenomenon attributable to a very thin film covering the main portion of the glaze. As far as could be determined, the color of the glaze under this film was independent of the firing atmosphere, but the thickness of the film did decrease with increasing oxygen. No film could be seen with the naked eye in a cross section of the glazes fired in 50 and 100% oxygen.

Mellor's hypothesis of the reduction of a small portion of the SnO_2 followed by its re-precipitation gives a possible explanation of the variations. The nature of the changes and the fact that they are surface effects seem to be strong indications of this. Although it has generally been accepted that scumming as such is produced only in a reducing atmosphere, it is possible that some decomposition of SnO_2 to soluble SnO could take place in a neutral atmosphere or one containing only a small percentage of oxygen. On the cooling cycle, then, the SnO dissolved near the surface would oxidize to precipitate SnO_2, which is more stable at the lower temperatures. This white SnO_2 would exert a diluting or lightening effect on the original chrome-tin color.

VII. Summary

(1) Variations in the composition of the firing atmospheres for the light green calcium-chrome glazes resulted in consistent changes in color from blue-green for 100% nitrogen to yellow-green for 100% oxygen. A possible mechanism for this color variation is a corresponding variation in the state of oxidation of the pigmentary calcium-chrome complex.

(2) For the vanadium-tin yellow glaze, variations in the firing atmosphere from pure nitrogen through a series of dilutions to pure oxygen resulted in a consistent change in the color of the glaze from yellow toward orange.

(3) The colors of the iron-chrome-zinc brown glazes were found to be independent of the composition of the atmosphere, possibly because of the formation of a stable $ZnO \cdot (Fe, Cr)_2O_3$ spinel.

(4) In the case of the chrome-tin pink and maroon glazes, a variation in lightness with atmosphere composition was found. Examination of cross sections of the glazes showed this variation to consist of the formation of a thin light-colored film over the main portion of the glaze when the firing was carried out in the more nearly neutral atmospheres. A possible explanation here is the reduction of a small amount of SnO_2 to soluble SnO on heating, followed by its reprecipitation near the surface on cooling.

Acknowledgment

The writer wishes to acknowledge the encouragement and advice of the late George H. Brown, Chairman of the Graduate Committee, and that of Charles J. Vitaliano; he also wishes to thank Laurence E. Kane for his personal interest and numerous suggestions in connection with the experimental part of the work.

This investigation was carried out under an Edward Orton, Jr., Ceramic Foundation Fellowship.

Department of Ceramics
Rutgers University
New Brunswick, New Jersey

INFLUENCE OF HUMIDITY ON DIELECTRIC PROPERTIES OF HIGH-FREQUENCY CERAMICS*

By Henry H. Hausner

Abstract

The dielectric properties of ceramics depend on composition, density, and surface conditions as well as many other factors. Humidity influences the dielectric properties to a large extent. These studies show that the amount of moisture depends on the compacting pressure and that the firing temperature has some influence on the dielectric properties in connection with relative humidity. Frequency and air pressure have an entirely different influence on the dielectric properties in relation to relative humidity.

I. Introduction

Although a great many papers have been published on dielectric properties of ceramic materials, many of these publications report on the same type of material. The figures for dielectric constant, dissipation factor, and loss factor, however, have shown discrepancies, and it is seldom clear why these figures vary so much and on what these divergences depend.

The dielectric properties of ceramic materials depend on (1) the polarizability, (2) the polarization of the particles of the respective materials, (3) the atomic polarization in the molecule, and (4) the electronic polarization in the individual atoms. Moullin[1] says that the atomic polarization in the molecule itself is very small as compared with the electronic polarization and therefore is difficult to determine. Smyth[2] be-

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1943 (White Wares Division). Received December 30, 1943.

(1944)

[1] E. B. Moullin, "Molecular Nature of a Dielectric," *Jour. Inst. Elec. Engrs.* [London], **86**, 113–28 (1940).

[2] C. P. Smyth, Dielectric Constant and Molecular Structure. Chemical Catalogue Co., Inc., 1931. 224 pp.

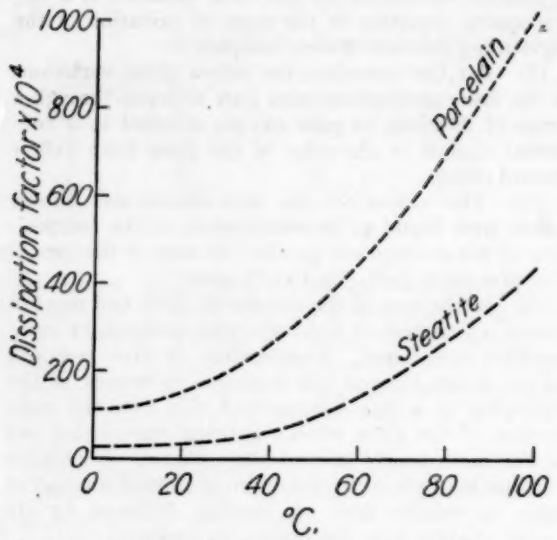

FIG. 1.—Dissipation factor vs. temperature; frequency 50 cycles per second (after Albers-Schönberg[4]).

lieves that the atomic polarization is unaffected by change of temperature. When ionized molecules, however, are arranged in a solid crystal lattice, Moullin[1] states that they contribute an atomic polarization which is subject to temperature variation and which depends on the lattice structure. A rise of temperature increases the lattice distances and decreases the attraction forces inside the molecule. The accuracy of these theories is unknown, but they give some explanation for the difficulties in explaining the dielectric phenomenon.

Apart from these theories, practical experience has proved that the dielectric properties of a ceramic material depend not only on the material itself or on the mixture of materials but also on grain size and compacting pressure and on the firing temperature, time, and cycle. They depend, furthermore, on the conditions of measurements, temperature, frequency, air pressure, and humidity. The writer will show why data published on exactly the same ceramic material often differ so greatly.

II. Factors Affecting Dielectric Properties

The influence of temperature on the dielectric properties of different ceramic materials has frequently been made the subject of studies. Figures 1 and 2 show the dissipation factors of different types of ceramic ware as a function of temperature. The amount of change occurring in the dissipation factor depends on the specific material used and also on the frequency of the measurements (Table I). Berberich and Bell[3] tested pure rutile ceramics, and their results on the dielectric constant and power factor (dissipation factor) are grouped together in Table I. These results show that temperature influences the power factor

[3] L. J. Berberich and M. E. Bell, "Dielectric Properties of Rutile Form of TiO_2," *Jour. Applied Physics*, **11**, 681–92 (1940).

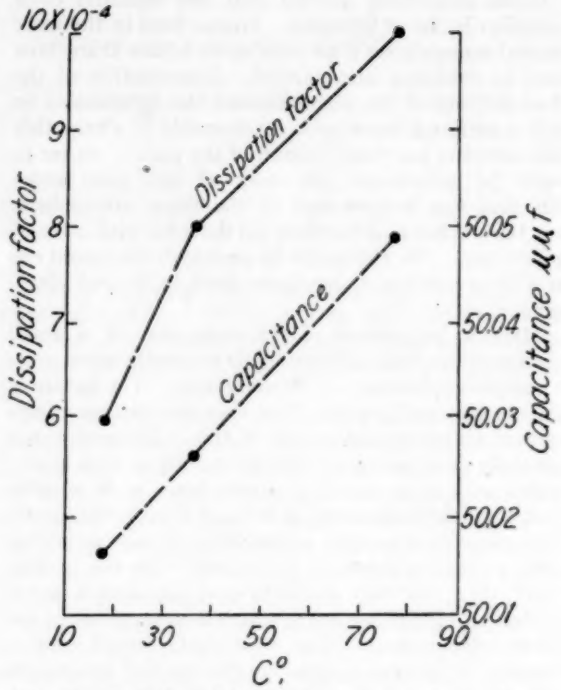

FIG. 2.—Variation of dissipation factor and capacitance of a rutile group material with temperature; frequency, 10^6 cycles per second (after Robinson[6]).

much more than the dielectric constant. The temperature dependency, moreover, is shown to be much greater at lower frequencies (60 cycles) than at high frequencies (10 kilocycles).

TABLE I

DISSIPATION FACTOR AND DIELECTRIC CONSTANT VERSUS TEMPERATURE (PURE RUTILE SPECIMENS)

(Frequency cycles)	Temp. (°C.) 30	60	100	125
	Dissipation factor			
60	0.009	0.02	0.07	0.145
1,000	0.006	0.009	0.02	0.045
10,000	0.003	0.005	0.009	0.025
	Dielectric constant			
60	104	103	106	117
1,000	103	100	100	101
10,000	102	99	97.5	97

The influence of frequency on the dielectric properties of ceramics or other insulating materials is well known. Data from Albers-Schönberg,[4] Keller,[5] and Robinson[6] are shown in Figs. 3 and 4. These graphs give the dissipation factor of steatite, mica, Bakelite, and rutile materials. The influence of frequency is

[4] E. Albers-Schönberg, Hochfrequenzkeramik (High-Frequency Ceramic Products). Theodor Steinkopff, Dresden, 1939. 177 pp.; *Ceram. Abs.*, **18** [11] 314 (1939).

[5] H. Keller, *Bull. Switzerland Elec. Assn.*, **25**, 718–19 (1934).

[6] W. G. Robinson, "Ceramic Insulations for High-Frequency Work," *Jour. Inst. Elec. Engrs.*, **86**, 570–77 (1940).

TABLE II

INFLUENCE OF HUMIDITY ON POWER FACTOR OF DIFFERENT DIELECTRIC MATERIALS AT 1000 KILOCYCLES

After firing	Power factor (10^4): In vacuum (24 hr.)	In 90% relative humidity (24 hr.)
(*a*) Natural ceramic firing surface		
8	6	9
4	2.5	13
12	9	18
(*b*) Natural ceramic firing surface (paraffin covered)		
3	2	5
4	3	11
(*c*) Natural ceramic firing surface (zinc covered)		
5	2	7
20	12	28
(*d*) Surface (ground)		
5	2	20
12	5	60
Quartz (ground)		
2	1.5	10
3	1.5	12
Mica		
2	1.7	4

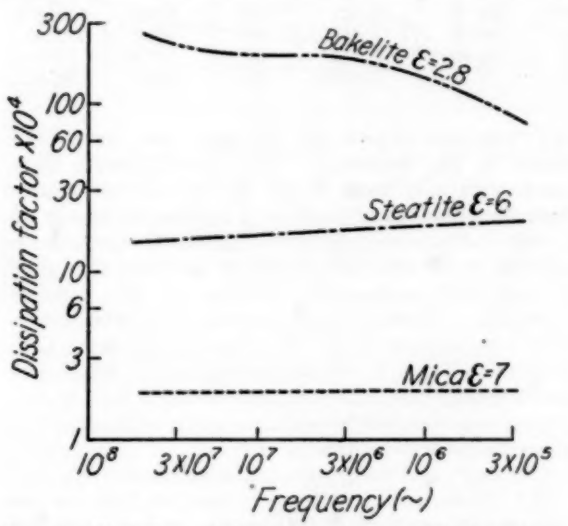

FIG. 3.—Variation of dissipation factor with frequency (after Keller[6]).

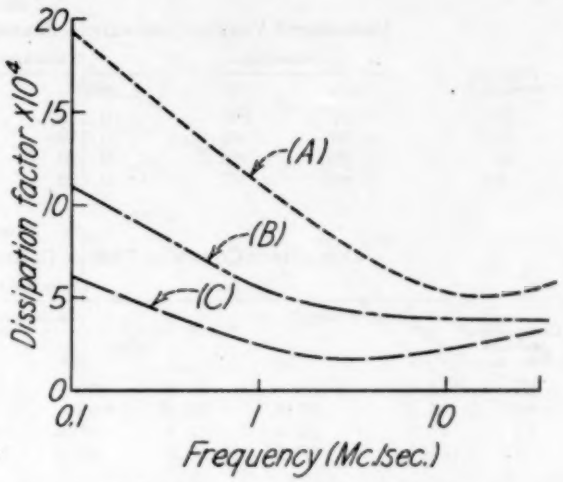

FIG. 4.—Variation of dissipation factor with frequency; 75% relative humidity; curves (*A*) steatite group material, (*B*) rutile group material (high permittivity), and (*C*) rutile group material (low temperature coefficient of permittivity); (after Robinson[6]).

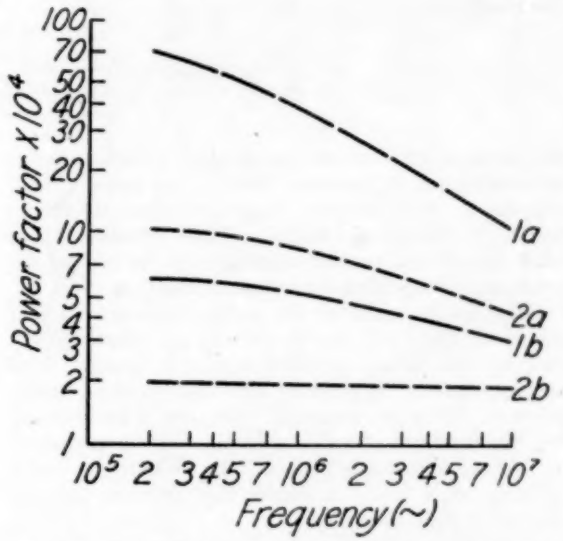

FIG. 5.—Power factor of two different specimens, Nos. 1 and 2; curve (*a*) sample in 90% relative humidity; curve (*b*) sample in vacuum (after Schwarz[7]).

particularly interesting in connection with the influence of humidity on dielectric properties as described in the following paragraph.

Few data have been published on the influence of humidity on the dielectric properties of ceramic ware. Investigations and experiments show that humidity often yields different figures for dielectric properties on the same materials. Schwarz[7] has published data on the influence of relative humidity on the dissipation factor of insulating materials. Figure 5 shows the dissipation factor of two different ceramic samples measured in 90% relative humidity and then in vacuum. There is no definite change of dissipation factor with different percentages of relative humidity for all materials; the influence of humidity varies with the materials, especially with the surface conditions of the materials. Different readings will be obtained if the ceramic material is measured (1) with its natural fired surface, (2) with this surface covered by paraffin or metals, or (3) with the surface ground.

Table II (according to Schwarz[7]) shows the dissipation factor of different ceramic materials under different surface conditions, measured (1) after firing, (2) after 24 hours in vacuum, and (3) after 24 hours in 90% relative humidity. This table also illustrates the fact

[7] H. Schwarz, *Electrotech. Z.*, **57** [1] 7–9 (1936).

TABLE III
DIMENSIONS VERSUS COMPACTING PRESSURE (RUTILE SPECIMENS, 7 GRAMS EACH)

Pressure (tons/in.²)	Diameter		Thickness		Surface area		Volume	
	(in.)	(%)	(in.)	(%)	(in.²)	(%)	(in.³)	(%)
20	1.92	100	0.118	100	6.50	100	0.342	100
16	1.90	99	0.119	101	6.38	98	0.338	99
12	1.885	98.2	0.120	101.8	6.30	97	0.334	97.8
8	1.865	97	0.122	103.3	6.18	95	0.334	97.8

TABLE IV
DIELECTRIC CONSTANT VERSUS COMPACTING PRESSURE (RUTILE SPECIMENS)

Compacting pressure (tons/in.²)	Dielectric constant (at 1 megacycle)									
	After firing		In desiccator				Relative humidity			
			18 hr.		130 hr.		70% (5 hr.)		55% (30 hr.)	
		(%)		(%)		(%)		(%)		(%)
20	15.52	100	16.2	100	16.31	100	16.4	100	16.15	100
16	15.2	97.8	15.87	98	15.95	97.8	16.1	98.4	15.95	98.9
12	15.2	97.8	15.8	97.5	15.80	97.5	16.0	97.0	15.86	98.1
8	15.4	99.2	15.6	96.3	15.46	94.8	15.63	95.3	15.55	96.2

TABLE V
DISSIPATION FACTOR VERSUS COMPACTING PRESSURE (RUTILE SPECIMENS)

Compacting pressure (tons/in.²)	Dissipation factor at 1 megacycle									
	After firing		In desiccator				Relative humidity			
			18 hr.		130 hr.		70% (5 hr.)		55% (30 hr.)	
		(%)		(%)		(%)		(%)		(%)
20	0.04	100	0.012	100	0.00605	100.0	0.021	100	0.0096	100
16	.045	112	.0114	95	.0058	95.5	.016	76	.0082	85.5
12	.047	117	.009	75	.0054	89.0	.012	57	.0073	76.0
8	.022	55	.004	33	.0046	77.0	.0086	41	.0065	68.0

that samples with ground surface show a minimum dissipation factor in vacuum, whereas the same ground samples in 90% relative humidity show maximum figures of dissipation factor. Thus it follows that whether or not a ceramic material is to be ground depends on its use either in vacuum or in air.

Experiments made by the author have proved that the effect of humidity, as described, was influenced not only by the surface of the test sample (natural fired surface, coated, or ground) but also by the forming pressure on the green sample. Because of the interesting development of rutile ceramic ware, experiments were made with rutile bodies. The dielectric constant of these rutile bodies is known to depend on the percentage of TiO_2 (Fig. 6).

III. Tests on Rutile Bodies

The tests were made on rutile bodies formed at different pressures from 8 to 20 tons per sq. in. The same quantity of material was used for each sample. After pressing, the samples were fired in a production tunnel kiln at a temperature of 2265°F. The shrinkage of the samples varied according to the respective compacting pressures. The diameter and thickness changes caused the volume to shrink to a lesser degree than the surface area. Table III shows actual figures of the diameter, thickness, volume, and surface area of the test samples, pressed at 8, 12, 16, and 20 tons per sq. in. and fired at 2300°F., as well as the percentage dimensions of the 20-ton per sq. in. sample. The samples were tested five times, after firing (conditioning in relative humidity of 60% for several hours), after they were placed in a desiccator for 18 hours, and again after another 130 hours in the desiccator. The measurements were made with a Q meter,* and the capacitance figures have been checked with a Twin-T impedance-measuring circuit.† These samples were tested after having been exposed to the open air at 70% relative humidity after 5 hours and again after 30 hours at 55% relative humidity. All measurements were made at a frequency of one megacycle. Table IV shows the dielectric constants and Table V, the dissipation factors. All figures in these tables are shown as the function of the forming pressures and of the five different states of humidity as described as test conditions.

Tables IV and V show the following results:

(1) There is a functional connection between the compacting pressure, the dielectric constant, and the dissipation factor, respectively. The influence of compacting pressure on the dielectric constant is insignificant compared with the influence on the dissipation factor. The dielectric constant as well as the dissipation factor increases with the rise of compacting pressure.

(2) The ability of this type of material to absorb moisture from the air depends on the compacting pressure. The influence of humidity is a function of the compacting pressure. It is surprising to notice that this influence increases with increasing forming pressure. Although the dissipation factor is influenced considerably by humidity, the dielectric constant is hardly affected at all.

* Boonton Radio Company.
† General Radio Company.

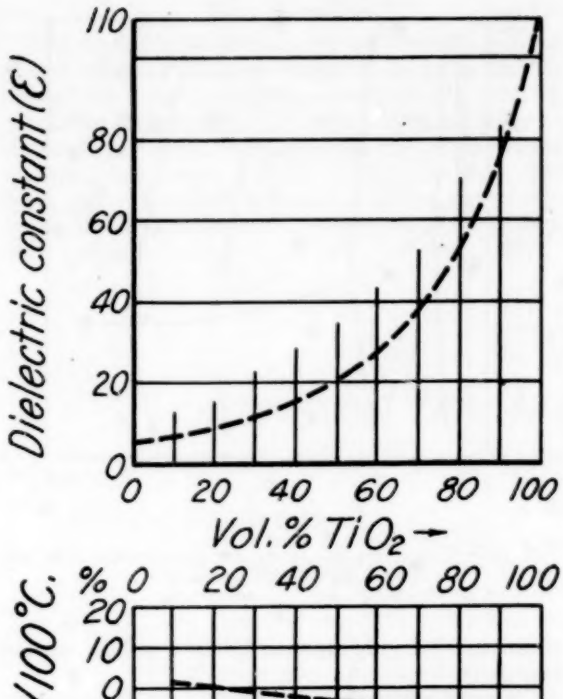

FIG. 6.—Dielectric constant (ε) and its temperature dependence $\left(\frac{\Delta\epsilon}{\epsilon}/100°C.\right)$ for rutile-containing ceramic bodies (after Werner Soyck, "Eigentümlichkeiten des dielektrischen Verhaltens rutilhaltiger Kondensator-Baustoffe," *Ver. Deut. Elecktrotech. Fachberichte*, pp. 129–32 (1935)).

TABLE VI

SURFACE RESISTIVITIES OF SOME COMMON SOLID INSULATORS

Material	Surface resistivity (megohms), relative humidity	
	At 25%	At 90%
Ivory	10,000	50
Celluloid	100,000	1000
Marble	100,000	10
Plate glass	100,000,000	20
Amber	1,000,000,000	100,000
Fused quartz	1,000,000,000	100
Ceresin	100,000,000,000	100,000,000,000

(3) The compacting pressure does not seem to influence the dissipation factor of samples in the dry state as much as it does on wet samples.

The knowledge of the influence of compacting pressure on dielectric properties in the wet or dry state may prove to be as important as the knowledge of shrinkage changes in volume and surface area influenced by the compacting pressure. Although no difference in the surface conditions was discernible, a change in the surface conditions seems to have occurred, resulting in a different surface resistance. Almost all changes of dissipation factors in different relative humidities

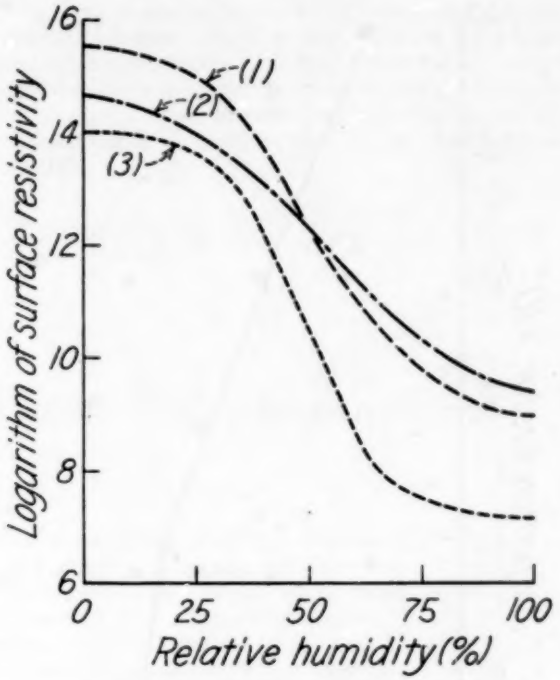

FIG. 7.—Surface resistivity vs. relative humidity; curves: (1) fused quartz, (2) glazed porcelain, and (3) plate glass.

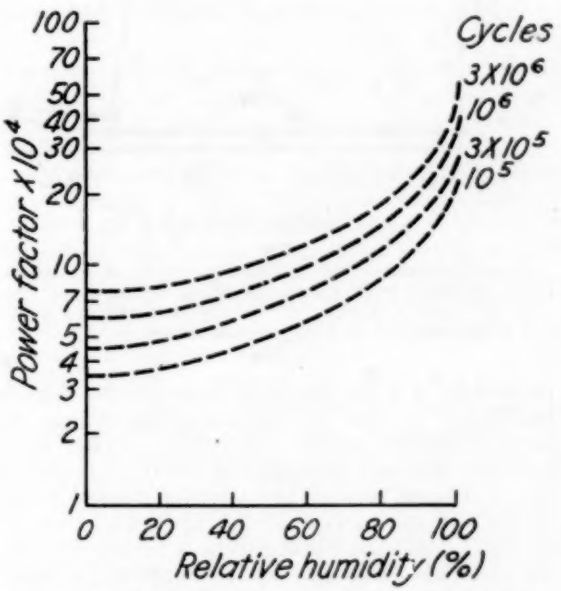

FIG. 8.—Power factor of ground specimens at different frequencies (after Schwarz[7]).

seem to the writer to be connected with the surface resistance. It is a small film of water or water vapor in the surface of the test sample which adds a parallel resistance to the condenser, the dissipation factor being indirectly proportional to this parallel resistance. Figure 7 shows the relation between the surface

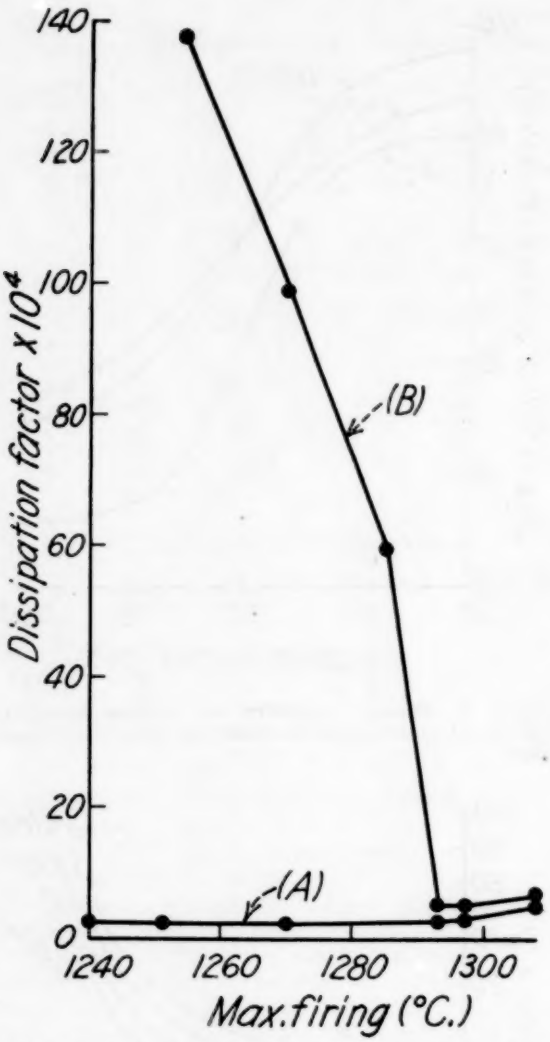

FIG. 9.—Variation of dissipation factor of a steatite group material with maximum firing temperature (frequency 1 mcy.); curve (*A*) in dry atmosphere; curve (*B*) in atmosphere of 75% relative humidity.

resistivities of a few glazed surfaces and the relative humidity.[8] In order to avoid misunderstandings, the standard definition of surface resistivity (as given in the American Standard Definitions of Electrical Terms[9]) is "the resistance between two opposite sides of a unit square" of the surface of the respective material. Table VI, published by the American Society for Testing Materials,[10] shows the surface resistivity of different materials at 25% and at 90% relative humidity. This table shows that a material with a high volume

[8] G. G. Smail, R. J. Brooksbank, W. M. Thornton, "Electrical Resistance of Moisture Films on Glazed Surfaces," *Jour. Inst. Elec. Engrs.* [London], **69**, 427–36 (1931).

[9] American Standard Definitions of Electrical Terms, p. 50. Published by Amer. Inst. Elec. Engrs., New York, 1942.

[10] American Society for Testing Materials, Nonmetallic Materials, General, Part III, 1942.

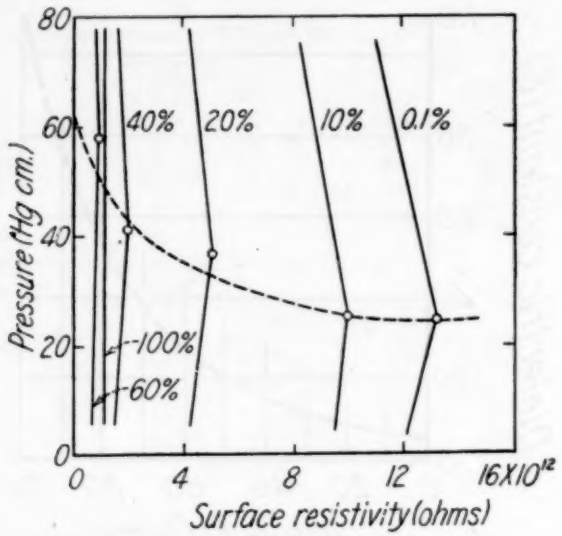

FIG. 10.—Surface resistivity vs. air pressure for different percentages of relative humidity.

resistivity does not necessarily have a high surface resistivity.

Figures 3 and 4 show the influence of frequency on the dissipation factor. A relation also exists between frequency, dissipation factor, and humidity. Figure 8 shows the dissipation factor of a ground ceramic sample, tested at four different frequencies and at different relative humidities.[7] Figure 8 also shows that the dissipation factor increases with the increase of frequency and humidity.

Several other factors are mentioned that are useful in determining the influence of humidity on dielectric properties. Figure 9 shows the variation of the dissipation factor of a steatite-group material with the maximum firing temperature. Tests were made both in dry atmosphere and in atmosphere of 75% relative humidity at a frequency of one megacycle. These data published by Robinson[6] show that, within a certain range, the firing temperature in no way influences the dissipation factor in the dry state of the sample, whereas the dissipation factor in the same range at 75% relative humidity increases considerably.

Air pressure is another factor neglected in most tests of ceramic materials. Figure 10 shows the relation between air pressure, humidity, and surface resistivity on a glazed surface.[8] There is a definite influence of air pressure on surface resistivity and consequently on the dissipation factor. This influence is in inverse proportion to the percentage of relative humidity. Smail, Brooksbank, and Thornton[8] show that there is a certain air pressure for each percentage of relative humidity when the surface resistivities are maxima. Although the influence of air pressure is not quite so essential as other factors, it might be of importance when ceramic material is used in airplanes under rapidly changing air pressures. The air pressure, in any case, should not be neglected in precision measurements of dielectric materials.

IV. Summary

The relation between humidity and dielectric properties of ceramics has been shown to be influenced by almost the same factors that determine the dielectric properties themselves. The influence of humidity on dielectric properties depends on the composition of the material, compacting pressure, firing temperature and time, and surface conditions; it is also dependent on the frequency of measurements, temperature and air pressure, and perhaps many other unknown components.

It is this great number of variables that influences the relation between humidity and dielectric properties and offers explanation for the fact that measurements on dielectric properties of the same type of ceramic material show entirely different results even though all measurements be made at exactly the same relative humidity.

Research Laboratories
General Ceramics and Steatite Corporation
Keasbey, New Jersey

CALCINATION OF TOPAZ ORE IN A ROTARY KILN*

By Gordon R. Pole

Abstract

Reports have indicated that calcined topaz might be useful as substitute material for Indian kyanite in high aluminous, mullite-type refractories. Tests were conducted to determine the value of calcining and defluorinating raw topaz. Fifteen tons of minus 1-in. topaz ore were calcined in a 25-ft. rotary kiln of 20-in. in inside diameter, at 2600° to 2950°C., with feed rate of 200 to 400 lb. per hour and feed retention in the kiln of 70 to 120 minutes. The best operating conditions were found to be 2700°F. and a feed rate of 300 lb. per hour at 0.90 r.p.m. of kiln rotation. The average fluorine content was 0.24% and the apparent porosity was 19%. A dust loss of 11% occurred during calcination, but no serious reduction in particle size occurred from the heat-treatment. It seems to be practicable, therefore, to calcine and defluorinate raw topaz in a rotary kiln and to obtain a product suitable for the manufacture of mullite-type refractories.

I. Introduction

In the manufacture of high-aluminous mullite-type refractories, a grog material of low apparent porosity and approximating mullite in composition ($3Al_2O_3 \cdot 2SiO_2$) is used in considerable quantities. Indian kyanite[1] has been used extensively for this purpose.

Approximately 18,000 tons of Indian kyanite have been imported annually into the United States; when calcined to 2780°F., it has an apparent porosity of about 15%, and a typical percentage analysis of an uncalcined sample is SiO_2 33.36, Al_2O_3 64.06, Fe_2O_3 0.71, TiO_2 1.52, CaO 0.24, MgO 0.04, and ignition loss 0.38.

Deposits of kyanite occur in the southeastern part of the United States, but the calcined American material expands more than the Indian ore. The calcined domestic kyanite has a higher apparent porosity, is more friable, and has a lower alumina content than Indian kyanite, containing 57 to 60% of Al_2O_3 as compared to 63 to 65% in Indian kyanite. Attempts to use calcined domestic kyanite as a grog material in highly aluminous mullite-type refractories have given poor results.[2]

Near the end of 1941, the Miscellaneous Minerals Branch of the Office of Production Management initiated a search for a substitute for Indian kyanite in refractories manufacture which indicated that calcined topaz had promising possibilities. The only known domestic topaz deposit large enough for commercial development as a source of material for the production of high-aluminous refractories occurs in Chesterfield County, S. C. A survey of this deposit made by the U. S. Geological Survey at the request of the Materials Division of the War Production Board revealed the presence of ample reserves to supply requirements of the refractories industry for several years. Descriptions of the topaz in this deposit have been published by Pardee, Glass, and Stevens[3] and by Stuckey and Amero.[4] Experiments by Bradley, Schroeder, and Keller[5]

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Refractories Division). Received December 3, 1943.

[1] (*a*) J. W. Greig, "Formation of Mullite from Cyanite, Andalusite, and Sillimanite," *Jour. Amer. Ceram. Soc.*, **8** [8] 465–84 (1925).
(*b*) W. J. Rees, "Use of Indian Sillimanite," *Trans. Ceram. Soc.* [England], **26** [2] 132–37 (1926–1927); *Ceram. Abs.*, **7** [2] 81 (1928).
(*c*) F. H. Riddle, "Andalusite as a Refractory," *Trans. Electrochem. Soc.*, **59**, 1–16 (1931); *Refrac. Jour.*, **7** [9] 436 (1931); *Ceram. Abs.*, **11** [1] 38 (1932).

[2] H. C. Harrison, "Cyanite-Clay Refractories, I," *Jour. Amer. Ceram. Soc.*, **9** [5] 257–71 (1926).

[3] J. T. Pardee, J. J. Glass, and R. E. Stevens, "Massive Low-Fluorine Topaz from Brewer Mine, South Carolina," *Amer. Mineral.*, **22** [10] 1058–64 (1937).

[4] J. L. Stuckey and J. J. Amero, "Physical Properties of Massive Topaz," *Jour. Amer. Ceram. Soc.*, **24** [3] 89–92 (1941).

[5] R. S. Bradley, F. W. Schroeder, and W. D. Keller, "Study of Refractory Properties of Topaz," *ibid.*, **23** [9] 265–70 (1940).

TABLE I

DATA FOR CALCINATION OF TOPAZ IN ROTARY KILN

	Operating period								
	T-17, T-18, T-19	T-4	T-6	T-10	T-11	Special T-14	Special T-15	Special T-16	Special T-20
Kiln operating time (hr.)	47	16	16	5	4	3	3	3	6
Oil burning rate (gal./hr.)	13	14	12	12	16	15	13	13	12
Kiln speed (r.p.m.)	0.90	0.55	0.81	0.81	0.90	0.76	0.76	0.76	0.90
Approx. time in kiln (min.)	70	120	70	70	70	85	85	85	70
	Kiln temp. (°F.)								
Recording radiation pyrometer	2705*	2815	2820	2865	2920	2950	2695	2605	2700
Firing head	2315	2225	2390	2400	2555	2310	2215	2150	2330
Exhaust head	1900	1895	1855	1820	1900	2260	2100	1950	1910
	Feed to kiln								
	Raw unscreened					Raw +10-mesh			Precalcined unscreened*
Total wt. (lb.)	14,153	3232	4726	1500	1600	900	906	909	1657
Rate (lb./hr.)	301	202	295	300	400	300	302	303	276
	Product from kiln								
Total wt. (lb.)	10,512	2493	3445	915	1022	687	575	608	1296
Rate (lb./hr.)	224	156	215	183	254	229	193	203	216
Fluorine (%)	0.24	0.51	0.51	0.15	0.26	0.15	0.26	0.31	0.20
Apparent porosity (%)	19.3	18.8	19.8	18.4	19.5	17.1	18.7	17.3	18.4

* Product from part of preliminary heating period and period T-4.

TABLE II

CHEMICAL ANALYSES, RAW MATERIALS, AND PRODUCTS

Sample No.*	Description of materials	Composition (%)						
		Moisture (110°C.)	SiO_2	AlF_3†	Al_2O_3‡	TiO_2	Fe_2O_3	F§
T-1	Composite of raw topaz shipment	0.1	34.6	22.0	41.6	0.6	0.5	14.9
T-5	Composite of raw topaz feed for period T-4		34.2	22.0	41.3			14.9
T-7	Composite of raw topaz feed for period T-6	0.1	32.9	22.2	42.6			15.1
T-12	Sample −10-mesh raw topaz fines	0.2	41.6	18.0	37.2	0.75	1.13	12.2
T-13	Sample +10-mesh raw topaz	0.1	34.2	21.0	42.6	0.69	0.63	14.3
T-2	Grab sample 1½-in. calcined lumps (preliminary operation)							0.71
T-3	Grab sample ¾-in. calcined lumps (preliminary operation)							0.82
T-4	Composite calcined topaz		29.8		65.1			0.51
T-6	" " "		30.4		67.8			0.51
T-8	Grab sample calcined topaz conglomerate lumps (period T-10)		39.7		53.9			0.20
T-9	Grab sample calcined topaz coarse lumps (period T-10)		27.5		69.4			0.46
T-10	Composite calcined topaz		30.7		68.5			0.15
T-11	" " "		32.8		61.3			0.26
T-14	Composite + 10-mesh calcined topaz		28.7		70.3			0.15
T-15	" " " " "		29.6		70.6			0.26
T-16	" " " " "		29.0		71.5			0.31
T-17	Composite calcined topaz		33.0		68.1			0.20
T-18	" " "		32.5		67.3			0.31
T-19	" " "		35.8		63.1			0.20
T-20	Composite recalcined topaz		31.0		68.7			0.20
T-21	Flue dust from rotary kiln		64.9	4.3	29.3			2.91

* Sample numbers correspond to operating periods in Table I.
† Computed from fluorine analysis, assuming all fluorine is combined as AlF_3 (see star footnote, p. 2).
‡ Computed as alumina not combined with fluorine as AlF_3.
§ Included in computed value for AlF_3.

on the fabrication of standard-size 9-in. brick made of raw and precalcined topaz gave encouraging results.

On the basis of the promising small-scale results, the War Production Board, in conjunction with the U. S. Bureau of Mines, requested the Tennessee Valley Authority at Wilson Dam, Ala., to conduct large-scale calcination tests in a rotary kiln on a 15-ton shipment of topaz ore.

II. Calcination Tests

The investigation consisted of calcination tests made on a 15-ton shipment of minus 1-in. raw topaz

TABLE III
SCREEN ANALYSES OF RAW AND CALCINED TOPAZ

Sample No.*	Cumulative percentage retained on 1 in.	½ in.	3-mesh	10-mesh	28-mesh	48-mesh	100-mesh
T-1	8.5	37.4	54.7	77.1	86.0	89.6	92.5
T-4	14.0	48.4	71.5	92.5	97.2	98.7	99.4
T-13	22.0	62.9	80.7	9[illegible].2	99.4		
T-14	15.0	60.2	82.0	99.2	99.8	99.9	
T-15	11.4	60.6	84.2	99.3	99.8	99.9	
T-16	9.9	51.6	77.5	99.1	99.8	99.9	
T-18	10.8	58.6	81.4	97.2	99.2	99.7	

* Sample numbers correspond to operating periods given in Table I and sample numbers in Table II.

TABLE IV
PHYSICAL PROPERTIES OF RAW AND CALCINED TOPAZ*

Sample No.†	Approx. diam. of test pieces (in.)	Calcination temp. (°F.)	Absorption (%)	Apparent porosity (%)	Specific gravity: Bulk	Specific gravity: Apparent
T-1	1–1.5	‡	0.39	1.36	3.45	3.50
T-2	1	2700	7.7	18.4	2.40	2.94
T-4	1	2800	7.6	18.4	2.41	2.96
	2	"	8.0	19.1	2.39	2.96
T-6	1	"	8.3	19.8	2.38	2.97
T-8	1.5	"	66.1	61.1	1.03	2.90
T-9	2	"	8.0	[illegible].2	2.42	2.99
T-10	1	2900	7.5	[illegible].1	2.42	2.95
	2	"	7.9	18.6	2.36	2.90
T-11	1	"	7.9	18.8	2.40	2.95
	2	"	8.6	20.2	2.37	2.96
T-14	1	"	6.4	15.6	2.50	2.98
	2	"	7.7	18.6	2.42	2.97
T-15	1	"	7.9	18.8	2.40	2.95
	2	"	7.9	18.6	2.37	2.94
T-16	1	2600	7.0	17.0	2.44	2.94
	2	"	7.6	17.6	2.34	2.84
T-18	1.5–2	2700	7.8	18.8	2.39	2.95
	1–1.5	"	8.5	20.2	2.36	2.99
T-19	1–1.5	2700	8.0	18.9	2.39	2.93
T-20	1–1.5	"	7.6	18.4	2.43	2.98

* Tested according to A.S.T.M. designation C 20–39T.
† Sample numbers correspond to operating periods given in Table I and sample numbers in Table II.
‡ Raw topaz.

from the Carolina Pyrophyllite Company of Staley, N. C., a subsidiary of the United Feldspar and Minerals Corporation. Chemical and screen analyses of the shipment were made on samples obtained by quartering six 100-lb. bags selected at random. The percentage chemical analysis was SiO_2 34.6, AlF_3* 22.0, Al_2O_3† 41.7, TiO_2 0.6, Fe_2O_3 0.5, F‡ 14.9, and moisture 0.1. The size distribution of the materials as indicated by the cumulative percentage retained was as follows:

	(% retained)		(% retained)
1 in.	8.5	28-mesh	86.0
½ in.	37.4	48-mesh	89.6
3-mesh	54.7	100-mesh	92.5
10-mesh	77.1		

Composite samples of the feed for two tests were analyzed as checks and showed agreement with these values, indicating that the shipment received was quite uniform in composition.

The topaz was calcined in a refractory-lined oil-fired rotary kiln. The kiln had an inside diameter of 20 in., a length of 25 ft., and a slope of 2 degrees (Fig. 1). Temperatures in the firing head and exhaust head were measured by thermocouples, and a recording radiation pyrometer was used to determine the interior temperature at a point about 6 to 8 ft. from the discharge end. Kiln operating temperatures were controlled on the basis of the radiation pyrometer measurement, which was influenced considerably by the flame from the burner. The temperatures are given in Table I as the average of hourly chart readings.

Topaz was first charged into the kiln at a rate of 200 lb. per hour and a kiln speed of 0.55 r.p.m. after a heating-up period of 7 hours. The kiln temperature as measured by the radiation pyrometer was 2650°F. It was found, however, that the kiln refractories and equipment were still absorbing heat and that steady operating conditions had not been reached. A sample of the calcined product from this period of operation contained 0.82% of fluorine. The operating tem-

* Computed from fluorine analysis assuming all fluorine combined as AlF_3 (see Rolf Schober and Erich Thilo, "Chemical Investigation of Silicates: X, Topaz, $Al_2SiO_4(F, OH, O)_2$, and Its Synthesis and a New Aluminum Oxide Containing Fluorine," *Ber. Deut. Chem. Ges.*, **73** [11] 1219–40 (1940); *Ceram. Abs.*, **20** [7] 177 (1941)).

† Computed as alumina not combined with fluorine as AlF_3.

‡ Included in computed value for AlF_3.

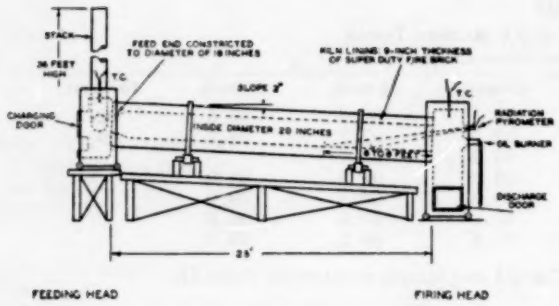

FIG. 1.—Rotary kiln used for calcination of topaz.

perature was raised to 2800°F. at the twelfth hour; at the sixteenth hour, steady conditions could be maintained, and the planned tests were begun.

The tests included studies of the calcination of topaz as received, of the plus 10-mesh screen fraction of this material, and of partially calcined topaz. Test conditions covered temperatures ranging from 2600° to 2950°F., feed rates ranging from 200 to 400 lb. per hour, and kiln speeds in the range of 0.55 to 0.90 r.p.m. (equivalent to an average approximate retention time in the kiln of 120 to 70 minutes as measured by the passage through the kiln of $1^1/_4$-in. refractory cubes introduced for this purpose). A series of short exploratory tests was made to determine the optimum conditions for operation. This type of operation was continued for a long period during which time a material balance was made and general observations of the operating characteristics were noted. A summary of these operating data is presented in Table I.

The chemical composition, screen analyses, and physical properties of the feed materials and products were determined and are shown in Tables II, III, and IV, respectively. Composite samples of the calcined products for each period were collected for chemical and screen analyses, and 1- to 2-in. pieces of the product were selected for porosity determinations.

In periods T–4 and T–6, tests were carried out to determine the effect of feed rates and retention time in the kiln on the properties of the product. The kiln temperature in these periods was maintained at about 2800°F. In period T–6, however, the feed rate was approximately 300 lb. per hour and the retention time was only 70 minutes, as compared to corresponding values of approximately 200 lb. per hour and 120 minutes for period T–4. These changes increased the production rate and reduced the fuel consumption per ton of product without appreciably affecting the fluorine content and apparent porosity of the product.

In period T–10, the temperature was increased to 2865°F.; the other operating conditions were the same as those of period T–6. The increased temperature reduced the fluorine content of the product from 0.51 (for period T–6) to 0.15% but had little effect on the other chemical and physical properties of the product. The calcined topaz from the kiln contained small balls (about 2 in. in size) of conglomerated fines held together by a binder of dark green glassy material. Except for the smaller particles, the material resembled small popcorn balls. The cooled balls were quite friable and could be broken by hand with difficulty. Analyses of the conglomerated balls and porosities of 2-in. solid chunks of grab samples (designated T–8 and T–9, respectively) obtained during this period of operation are reported in Tables II and IV, respectively. The analyses show that the conglomerated product had a higher silica content and was much more porous than the regular product from period T–10. In subsequent grinding and handling operations, the conglomerated product probably could be reduced easily to fines with an apparent porosity approaching that of the lump material.

Period T–11 represented an attempt to increase the output of the kiln. The feed rate was increased to 400 lb. per hour and the temperature was increased to about 2920°F. Under these conditions, the kiln tended to "back feed" at the charging end, and it was necessary to recharge large amounts of topaz that collected in the flue head. Feed rates much above 300 lb. per hour appeared to exceed the capacity of the kiln.

In periods T–14, T–15, and T–16, a series of special tests was made. The kiln feed for these tests was obtained by passing the topaz over a 10-mesh vibrating screen and charging to the kiln only the plus 10-mesh fraction. Analyses of these fractions are given in Tables II and III. The feed rate for all tests was 300 lb. per hour, and the kiln rotation was adjusted so that the charge was retained in the kiln about 85 minutes. The kiln temperatures for periods T–14, T–15, and T–16 were about 2950°, 2700°, and 2600°F., respectively. Between runs, the kiln was cleared as completely as possible. The results of this series of tests indicate that the fluorine content varies as an inverse function of the temperature; the fluorine content of the material in each period was lowered to less than 0.5%. There was no significant trend in the apparent porosities in the tests.

From the exploratory tests, it was concluded that the optimum conditions for calcination of the topaz in the laboratory kiln were a feed rate of 300 lb. per hour, a feed retention time of 70 minutes, and a kiln temperature of approximately 2700°F. The test conducted during periods T–17, T–18, and T–19, therefore, was carried out under these conditions. The test period was 47 hours. The product obtained during this extended period appeared to be uniform, the fluorine content varying from 0.20 to 0.31% and the porosities ranging from 18.8 to 20.2%.

Estimates of the dust losses and the loss by volatilization were made for periods T–17, T–18, and T–19. The results indicate that approximately 11% of the feed was lost as dust and about 17% was lost by volatilization. The volatilization loss approximates the loss of 16% reported by Stuckey and Amero.[4]

During the final period of operation (period T–20), a test was made to determine the effect of the recalcination of topaz that had not been defluorinated below 0.5%. The feed material was topaz that had been fed before the kiln had reached temperatures high enough to calcine the material as completely as was desired. The test was carried out under the previously deter-

Dust and volatilization losses for T-17, T-18, and T-19.

ASSUMPTION: No Al_2O_3 volatilized.

Data	
Total wt. topaz fed to kiln (lb.)	14,153
Total wt. product (lb.)	10,512
Total Al_2O_3 content of raw topaz (%)	55.0
Al_2O_3 content of product (%)	66.2

CALCULATIONS	
(1) Wt. raw topaz equivalent to product (lb.) $= \left(\frac{66.2}{55.0} \times 10{,}512\right)$	12,653
(2) Raw topaz lost as dust (lb.) = (14,153 − 12,653)	1,500
(3) Total material lost as dust and by volatilization (lb.) = (14,153 − 10,512)	3,641
(4) Total material lost by volatilization (lb.) = (3641 − 1500)	2,141
(5) Dust loss (%) $= \left(\frac{1500}{14{,}153} \times 100\right)$	10.6
(6) Volatilization loss (%) $= \left(\frac{2141}{12{,}653} \times 100\right)$	16.9

mined optimum operating conditions. The fluorine content of the product from the second calcination was 0.20%. The product appeared similar in every respect to material produced by a single calcination under the same operating conditions. Apparently no reduction in quality of the final product would result after recalcination.

III. Examination of Kiln After Operation

When the calcination experiments were completed, the kiln was allowed to cool and the lining was examined. No evidence of deterioration was found. The surfaces of the superduty brick were thoroughly vitrified, and fine grains of calcined topaz were firmly embedded in the surface. A small ring of partially calcined conglomerated topaz was found adhering to the wall approximately 16 ft. from the hot end. The ring was quite friable and broke away readily when poked with a steel rod.

The flue head was coated with $^1/_2$ in. of extremely fine white powdery material. No analysis of this material was made, but material similar in appearance has been reported by Stuckey and Amero[4] to be silica.

The horizontal section of the flue leading to the stack was partially plugged with a gray dust that appeared to be a mixture of fine topaz and silica, similar to the material found in the flue head; a chemical analysis of the material supported this conclusion (see analysis T-21 in Table II).

IV. Discussion and Conclusions

Based on the 48-hour test under the optimum conditions used, the rotary kiln seems to offer a practicable means for calcining and defluorinating topaz ore. Defluorination to less than 0.5% can be effected by a calcination procedure that can be maintained without difficulty. There appears to be no problem with kiln corrosion or other unusual deterioration of equipment. The feed showed no pronounced tendency to stick or ball in the kiln. The dust losses (about 11%) are believed to be considerably higher than would be experienced in full-scale operation because the ratio of the cross-sectional area of the kiln to that of the feed in the kiln would be considerably greater in a larger kiln. This increase would result in a lower velocity through the kiln for the fuel combustion products with consequent reduction in dust loss. Operation on a larger scale would result also in a lower fuel consumption per ton of product. The screen analyses of the minus 1-in. topaz ore and product also showed that the larger screen fractions (1 to $^1/_2$ in.) were affected most by calcination in reduction in particle size.

The product appears to be well suited to the fabrication of high-grade mullite-type refractories.[6] The apparent porosity of the product is considerably greater than that of Indian kyanite (19 to 20% as compared to 14.6%, respectively). Commercial grades of high-alumina brick made from diaspore and from bonded synthetic mullite, however, have porosities varying from 20 to 30%, and many of the best grades of bonded or wet-cast refractories used as flux blocks for glass-making furnaces have apparent porosities of 20 to 25%. The higher porosity of the calcined topaz as compared with that of Indian kyanite is believed to be no serious detriment. The tests showed that a product with an alumina content as high as 67 to 70% could be produced. This content compares with 63 to 65% and 57 to 60% of alumina for Indian kyanite and high-grade domestic kyanite, respectively. The higher alumina content of the calcined topaz should be an advantage in the manufacture of mullite-type refractories because it is closer to that of mullite, which contains 71.8% of Al_2O_3. The small amounts of fluorine remaining in the calcined product might actually be beneficial as a mineralizer in promoting "mullitization" when the topaz is mixed with other bonding materials, such as clays, for use as refractories.

Acknowledgment

H. F. Carl of the U. S. Bureau of Mines and J. E. Boyd of the United Feldspar and Minerals Corporation were present during this investigation and participated in the experimental work. S. E. Barr, R. M. Dasher, and J. E. Rothfleisch of the TVA Department of Chemical Engineering also assisted in the work.

TENNESSEE VALLEY AUTHORITY
WILSON DAM, ALABAMA

[6] T. N. McVay and Hewitt Wilson, "Substitution of Topaz, Domestic Kyanite, and Synthetic Mullite-Corundum for India Kyanite, I–III," *Jour. Amer. Ceram. Soc.*, **26** [8] 252–66 (1943).

CALCULATION OF SURFACE TENSIONS OF GLASSES*

By K. C. Lyon

Abstract

Factors have been derived for the calculation of the surface tensions of glasses from their compositions at temperatures of 1200° and 1400°C. The nine oxides evaluated are those commonly found in significant amounts in glass compositions. The surface tension of a glass may be calculated with a fair degree of assurance from its composition to within about 4 dynes per cm.

I. Introduction

The literature on glass offers factors for the calculation of many of its physical properties. Among these factors are thermal expansion, density, refractive index, dispersion, viscosity, and others. The measurement of the surface tensions of molten glasses has been given serious experimental consideration in recent years with the result that a fair number of values for this property determined on a wide variety of glass compositions may be found in the literature.

Various writers have discussed the effects of surface tension in the glassmaking process, the fining of glass, the persistence of cords, the corrosion of refractories, and the forming of the finished product.

Babcock[1] has proposed factors for calculating the change in surface tension between one glass composition and another, based on molecular composition at 1400°C. Dietzel[2] has presented values for the calculation of the surface tension of glasses from their weight percentage composition at 900°C., with provision for adjusting the final result to other temperatures.

The present work reports the results of the determination of constants for calculating surface tensions of glasses at 1200° and 1400°C., based on the data from about seventy-five glasses reported in the literature readily available to the author. The factors so derived are of the same order of magnitude as those given by Dietzel, and a few of them are in excellent agreement by extrapolation. The glasses studied include in their analyses Na_2O, K_2O, Fe_2O_3, Al_2O_3, B_2O_3, CaO, MgO, BaO, SiO_2, and SO_3 in various combinations. The recurrence of several of these oxides in significant amounts in a number of glasses warrants confidence in the values calculated for them. Less certainty may be attached to factors for oxides which occur in significant amounts in only one or two glasses.

II. Data

The sources and type of data used for this study are listed in Table I.† The 1400°C. values from Badger, Parmelee, and Williams[3] were obtained by subtracting 1 dyne per cm. from the reported 1350° value.‡ The 1200° and 1400°C. values from Babcock[1] were determined by calculating the linear relation between surface tension and temperature by the method of least squares from the data given. Values from Parmelee and Harman[4] were read from graphs presented in their reports; those from Parmelee and Lyon[5] were calculated from the equations given in their paper; and Keppeler[6] reported values at 1400°C. The values given by Silverman[7] for 1250°C. were adjusted to 1200°C. by adding 1 dyne per cm. to the reported values.

The compositions of the glasses were taken as stated by the various sources. When these reported compositions totaled less than 99%, they were adjusted in a few instances to 100% by proportion; when R_2O_3 was reported, it was taken to be Al_2O_3.

III. Procedure

The data available presented fourteen compositions, which were composed essentially of soda, lime, and silica and in which the weight ratio of SiO_2 to Na_2O approached or exceeded 4. The compositions and the reported surface-tension values of these glasses were averaged to obtain a single composition and a corresponding surface-tension value. Preliminary studies revealed the approximate magnitude of the effect

* Presented at the Glass Division Autumn Meeting, September 15, 1943. Received October 20, 1943.

[1] C. L. Babcock, "Surface-Tension Measurements on Molten Glass by Modified Dipping-Cylinder Method," *Jour. Amer. Ceram. Soc.*, **23** [1] 12–17 (1940).

[2] A. Dietzel, "Practical Importance and Calculation of Surface Tension in Glasses, Glazes, and Enamels," *Sprechsaal*, **75** [82] 82 (1942); *Chem. Abs.*, **37** [1] 2422 (1943).

† It will be noted that the majority of these samples are from the Department of Ceramic Engineering of the University of Illinois and the Research Laboratory of the Owens-Illinois Glass Company.

[3] A. E. Badger, C. W. Parmelee, and A. E. Williams, "Surface Tension of Various Molten Glasses," *Jour. Amer. Ceram. Soc.*, **20** [10] 325–29 (1937).

‡ Although the temperature coefficient of surface tension varies with glass composition, it is negative and of the order of 0.01 to 0.02 dyne per cm. per °C. for the glasses studied; a 50°C. correction amounts to approximately 1 dyne per cm.

[4] (*a*) C. W. Parmelee and C. G. Harman, "Surface Tensions of Molten Glasses: II, Surface Tensions of Soda-Lime-Silica Melts," *Univ. of Ill. Eng. Expt. Sta. Bull.*, No. 311, pp. 29–47 (1939); *Ceram. Abs.*, **18** [11] 295 (1939).

(*b*) C. W. Parmelee and C. G. Harman, "Effect of Alumina on Surface Tension of Molten Glass," *Jour. Amer. Ceram. Soc.*, **20** [7] 224–30 (1937).

[5] C. W. Parmelee and K. C. Lyon, "Surface Tensions of Molten Glasses: I, Surface Tension of Molten Glass," *Univ. of Ill. Eng. Expt. Sta. Bull.*, No. 311, pp. 5–27 (1939); *Ceram. Abs.*, **18** [11] 224–30 (1939).

[6] Gustav Keppeler, "Surface Tension of Glass," *Jour. Soc. Glass Tech.*, **21** [83] 53–60 (1937); *Ceram. Abs.*, **17** [8] 275 (1938).

[7] W. B. Silverman, "Surface Tension of Glass and Its Effect on Cords," *Jour. Amer. Ceram. Soc.*, **25** [6] 168–73 (1942).

TABLE I
SURFACE-TENSION DATA EMPLOYED

Authority*	Composition determined	Temp. (°C.)	Composition	No. of glasses
Babcock[1]	Chemical analysis	1150–1400	SiO_2, Al_2O_3, CaO, MgO, Na_2O, SO_3	24
Badger, Parmelee, and Williams[3]	Calculated	1200 and 1350	SiO_2, Fe_2O_3, Al_2O_3, B_2O_3, CaO, MgO, BaO, Na_2O, K_2O	16
Parmelee and Harman[4(a)]	"	1100–1400	SiO_2, CaO, Na_2O	15
Parmelee and Harman[4(b)]	"	1200–1400	SiO_2, CaO, Al_2O_3, MgO, Na_2O	4
Parmelee and Lyon[5]	Chemical analysis (adjusted)	1100–1300	SiO_2, R_2O_3, B_2O_3, Na_2O	7
Keppeler[6]	Partial analysis (calculated)	1400	SiO_2, R_2O_3, B_2O_3, CaO, Na_2O	6
Silverman[7]	Not stated	1250	SiO_2, R_2O_3, CaO, MgO, BaO, Na_2O, K_2O, SO_3	11

* Babcock and Silverman used the dipping-cylinder method; Badger and Parmelee and their co-authors and Keppeler used the maximum bubble-pressure method.

TABLE II
EFFECT OF 1% OXIDE ON SURFACE TENSION OF GLASS IN WHICH RATIO SiO_2 : Na_2O EXCEEDS 3.25

Oxide	Dynes/cm. 1200°C.	Dynes/cm. 1400°C.
SiO_2	3.25	3.24
Fe_2O_3	(4.5)*	(4.4)
Al_2O_3	5.98	5.85
B_2O_3	0.23	−0.23
CaO	4.92	4.92
MgO	5.77	5.49
BaO	(3.7)	(3.8)
Na_2O	1.27	1.12
K_2O	(0.00)	(−0.75)

* Values in parentheses are intended to be indicative of order of magnitude only; they are present in significant amounts in very few of the glasses treated.

on surface tension of the minor constituents (Al_2O_3, MgO, and SO_3) of this average glass. The average surface tension was corrected for the presence of these minor constituents to give a composition in terms of Na_2O, CaO, and SiO_2 and an equivalent surface tension.

A series of arbitrary values was chosen for silica and another for lime. By using the members of these two series in the average glass, it was possible to solve for values representing the effect of soda on surface tension, and the result obtained was dependent on the particular combination of lime and silica factors employed. Each set of related factors so determined was applied to each of the fourteen glasses individually, and the surface-tension value calculated by their use was compared with the observed surface-tension value. The factors for soda, lime, and silica selected for study were those which resulted in the least standard deviation when tried in the individual glasses and which also exactly calculated the surface tension of the composition represented by the average of the fourteen glasses.†

The factors for MgO and Al_2O_3 were determined similarly for twenty-five glasses which contained these oxides in addition to the soda, lime, and silica. The average composition in this case was corrected by

† Algebraic solution (regression coefficients) of the fourteen equations for the three unknowns resulted in an expression which included a rather large negative constant, whereas the method adopted here reduced such a constant to zero.

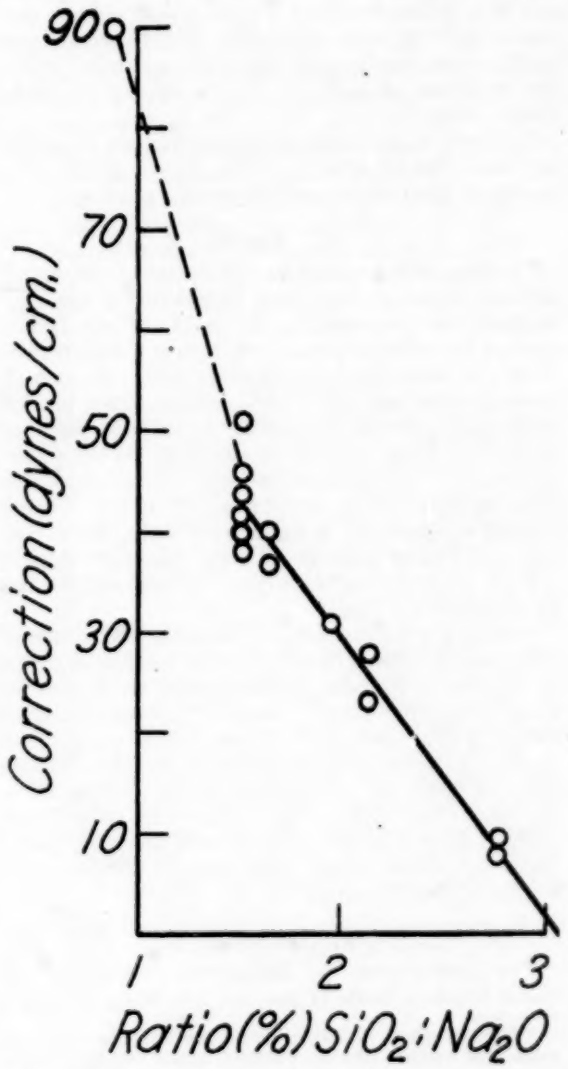

Fig. 1.—Correction for calculated surface tensions at 1200° to 1400°C. for soda-lime-silica glasses.

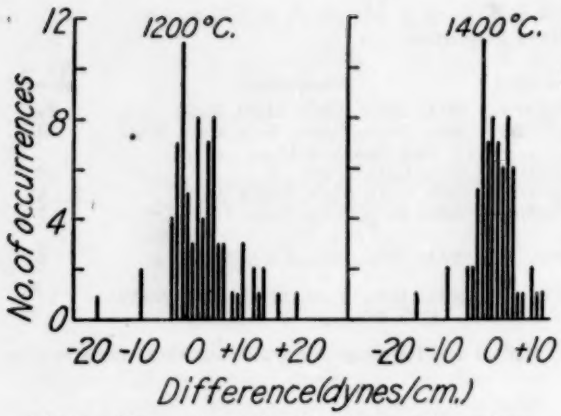

Fig. 2.—Observed-calculated surface-tension values.

use of the factors already determined for Na_2O, CaO, and SiO_2, arbitrary values for Al_2O_3 were chosen, and factors for MgO were calculated. Final selection was based on the combination giving the minimum standard deviation when tested in the twenty-five individual glasses.

With five of the oxide factors determined as stated, the remainder reported in Table II was found by a process of substitution and solution for unknowns.

IV. Results

The factors derived for the calculation of the surface tensions of glasses from their weight-percentage compositions are presented in Table II. These factors seem to be valid for glasses which have a weight ratio of SiO_2 to Na_2O greater than about 3.25. An over-all correction for soda-silica and soda-lime-silica glasses, which have lower ratios of SiO_2 to Na_2O, is provided in Fig. 1. These corrections are based on the results reported by Parmelee and Harman[4(a)] on glasses whose ratios of SiO_2 to Na_2O varied from 0.97 to 4.0. Such a correction apparently is unnecessary if the glasses contain appreciable amounts of B_2O_3, inasmuch as they are not applicable to the sodium borosilicates studied by Parmelee and Lyon.[5]

Because the work of Badger, Parmelee, and Williams[3] gives surface-tension data for glasses containing oxides in addition to the nine evaluated here, the factors for these oxides for 1400°C. may be approximated by adding 2 dynes per cm.* to their values reported for 1350°C., calculating the surface tensions for the factors given in Table II, and attributing the differences to the additional oxide. The factors for 1200°C. are yielded when a similar procedure is followed, and 3 dynes per cm. are added to the Badger, Parmelee, and Williams 1200°C. values.

V. Discussion

The factors given by Dietzel[2] for 900°C. for the oxides listed in Table II are SiO_2 3.4, Fe_2O_3 4.5, Al_2O_3 6.2, B_2O_3, 0.8, CaO 4.8, MgO 6.6, BaO 3.7, Na_2O 1.5, and K_2O 0.1. Between these and the factors recommended here, the agreement (by extrapolation) is good for Na_2O, Al_2O_3, and B_2O_3. There is fair agreement for Fe_2O_3. In view of the amount of silica found in most glasses, the difference between the two values for silica is important. In his paper on surface tension and cords, Silverman[7] shows that a fiber of fused silica will dissolve in 300 seconds in a glass whose surface tension was found to be 326 dynes per cm. at 1250°C. From the results on some of the other glasses studied by Silverman, it would seem that if silica has a surface tension of the order of 340 dynes per cm., as given by Dietzel, its solution in the base glass would have taken much longer. It is believed, therefore, that the lower value for silica reported here is more nearly correct than Dietzel's value. The differences in values for CaO and MgO between Dietzel and those given in Table II may be explained in terms of their dependence on the silica value.

With respect to the factors given in Table II, the order of their magnitude seems to be correct. The temperature gradient indicated for MgO and Al_2O_3 may be somewhat excessive compared with SiO_2 and CaO, but it is based on the data available. The values for BaO increase with increasing temperature instead of the reverse as might be anticipated. It should be pointed out that the data from which this value was calculated (sample No. 10 of Badger, Parmelee, and Williams[3]) show an unusually small temperature gradient. The calculation of the surface tension of glass probably can be carried out with satisfactory accuracy without knowledge of the exact effect of temperature on the individual factors. If it is desired to extrapolate the values for any appreciable temperature range, however, the specific temperature effects should be accurately known.

Although some of the glasses used in this study were reported to contain fractional percentages of SO_3, no attempt was made to evaluate its effect on surface tension. Throughout this work, it was treated as having a value of zero.

The graphs of Fig. 2 show the difference between the values reported for the glasses studied and the surface tensions of these glasses calculated by use of the factors given in Table II. Of the seventy-seven glasses calculated at 1200°C., fifty-six showed a variation from the observed value of 4 dynes per cm. or less, with an average deviation of 4.4. Of the seventy-two glasses at 1400°C., fifty-nine showed a variation from the observed value of 4 dynes per cm. or less, with an average deviation of 4.4. The tendency of many glasses to show a −3 dynes difference in Fig. 2 is due, in part, to an apparent systematic difference of this amount in the Badger, Parmelee, and Williams[3] series. There seems, furthermore, to be a systematic difference between the Silverman[7] observed values and the calculated values averaging about +12 dynes per cm. This difference is indicated in the 1200°C. portion of Fig. 2. There is nothing in the original papers from these two sources to indicate a reason for these seeming systematic differences.

* Factors given in Table II, on the average, will give calculated surface-tension values 3 dynes per cm. higher than those reported by Badger, Parmelee, and Williams[3]; the 2-dyne correction suggested for deriving the 1400° values also includes a temperature correction.

There are also some rather large discrepancies in the high-soda glasses of the Parmelee and Lyon[5] series of sodium borosilicates. The calculated result in these glasses is higher than the observed surface tension; according to the chemical analyses, these glasses appear to have picked up large amounts of R_2O_3 in their preparation. Although the results of the chemical analyses cannot be questioned, it may be pointed out that the surface tension calculated from the composition to be expected from the batch used is in much better agreement with the observed surface tension than that calculated from the results of the analytical determination. Because the factor for B_2O_3 performs satisfactorily in five of the Keppeler[6] and two of the Badger, Parmelee, and Williams[3] glasses, it would seem that the discrepancy in a few of the Parmelee and Lyon[5] glasses should not necessarily be ascribed to an error in the value for this oxide factor.

VI. Summary

The results of a study of the literature reporting the determination of surface tensions of molten glasses indicate that this property may be computed as an additive function of composition to within about 4 dynes per cm. at 1200° and 1400°C.

ARMSTRONG CORK COMPANY
MILLVILLE, NEW JERSEY

OPTICAL GLASS FROM THE VIEWPOINT OF THE LENS DESIGNER*

BY R. KINGSLAKE

ABSTRACT

The glass used in the manufacture of lenses must be chemically stable and substantially free from bubbles, color, and striae. The lens designer is then concerned only with the refractive index and the dispersive power of the available glasses. Because practically every new lens must be achromatic, the positive elements used in it must be made from glass having a low dispersive power; the negative elements must have a relatively high dispersive power. The choice of refractive index is determined by many conflicting factors because the only "tools" available to the designer for the correction of many different aberrations are the radii of curvature of the lens surfaces, the thicknesses and air spaces, and the refractive indices of the glasses. The range of optical glasses commercially available and the reasons underlying the designer's selection of glass for different kinds of lenses are discussed.

I. Introduction

To the lens designer, optical glass is merely a convenient transparent material having certain specified values of refractive index and dispersion from which it is possible to make lenses. He is not interested in its chemical composition, the method of its manufacture, or its chemical or physical properties. He assumes that the glass which is available to him is colorless, stable to atmospheric weathering, and free from obvious physical defects, such as striae and large bubbles. These factors, therefore, do not come within the scope of the present paper.

A particular type of optical glass may be defined by stating its two fundamental optical properties, namely, "refractive index"† and "dispersive power."‡ The refractive index, n, is a measure of the ability of any material to bend a ray of light as it enters or leaves the surface of that material, and the dispersive power, w, is a measure of the amount by which the various colors of the spectrum are spread out when a ray of white light passes through a lens or prism made of the material.

II. Achromatism

Dispersion of glass is a regrettable attribute to the lens designer because it merely causes the image to be colored and indistinct, and a great amount of time is spent in trying to overcome it. In the usual positive lens system, a strong positive lens of low-dispersion glass must be combined with a weaker negative lens of high-dispersion glass. Each element then contributes its share to the over-all power as well as to the over-all dispersion, and by taking care to make the dispersion contributions equal and the power contributions unequal, it is possible to design an achromatic lens having any desired positive or negative power.

Every positive lens that is designed, therefore, must contain one or more positive elements of low-dispersing glass and also one or more negative elements of high-dispersing glass. The precise distribution of dispersive powers among the various elements in a lens is often determined by other considerations because the same ultimate chromatic correction may obviously be

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Glass Division). Received April 12, 1944.

† Strictly, the mean refractive index, n_D, of a material is the ratio of the velocity of light of wave length 0.5893 μ (sodium light) in air to its velocity in the material. The degree of refraction of a ray at a surface separating a material, a, from a different material, b, is given by the law of refraction, $n_a \sin I_a = n_b \sin I_b$; I represents "angle of incidence" between the ray and the normal to the surface at the point of incidence.

‡ Dispersive power is defined by the ratio $\frac{n_F - n_C}{n_D - 1}$; n_F and n_C are, respectively, refractive indices of material for F (0.4861) and C (0.6563) lines in the hydrogen spectrum. Optical glass catalogues generally state only the reciprocal of the dispersive power, denoted by symbol V or ν.

TABLE I

OPTICAL GLASS TYPES NOW BEING MANUFACTURED IN THE U.S.A.

(In order of increasing dispersive power)

Manufacturer*	Name	n_D	w (%)	$V = \frac{1}{w}$
Pitt	BSC-1	1.4978	1.493	67.0
BL+	BSC-2	1.5170	1.550	64.5
BL+	BSC-1	1.5110	1.575	63.5
Pitt	C-2	1.5000	1.623	61.6
BL	C-2	1.5125	1.653	60.5
Corn	SK-16	1.6203	1.658	60.3
BL+	LBC-1	1.5411	1.669	59.9
BL	C-3	1.5178	1.678	59.6
BL+	DBC-1	1.6110	1.701	58.8
BL+	C-1	1.5230	1.706	58.6
BL+	LBC-2	1.5725	1.742	57.4
BL+	DBC-3	1.6109	1.748	57.2
BL	LBC-3	1.5725	1.761	56.8
Pitt	C-3	1.5013	1.770	56.5
EK	EK-11	1.6968	1.783	56.1
Corn	SK-18	1.6384	1.802	55.5
BL+	DBC-2	1.6170	1.818	55.0
Pitt	CF-2	1.5254	1.825	54.8
Pitt	LBF-1	1.5710	1.825	54.8
BL	EDBC-1	1.6150	1.852	54.0
BL+	LBF-1	1.5880	1.873	53.4
BL	CF-1	1.5286	1.938	51.6
BL	LBF-2	1.5621	1.961	51.0
Pitt	CF-1	1.5230	1.980	50.5
Pitt	BF-1	1.6160	2.033	49.2
BL+	ELF-3	1.5414	2.105	47.5
Corn	BaF-10	1.6699	2.119	47.2
EK	EK-33	1.7551	2.119	47.2
BL+	BF-1	1.5838	2.174	46.0
BL	ELF-2	1.5497	2.183	45.8
EK	EK-32	1.7445	2.183	45.8
BL	ELF-1	1.5585	2.198	45.5
BL	BF-2	1.6053	2.294	43.6
BL+	LF-4	1.5751	2.336	42.8
BL+	LF-1	1.5725	2.353	42.5
BL+	LF-3	1.5750	2.415	41.4
BL	LF-2	1.5795	2.439	41.0
Pitt	DBF-1	1.6560	2.469	40.5
BL	DBF-1	1.6170	2.597	38.5
BL+	DF-1	1.6050	2.632	38.0
BL+	DF-2	1.6170	2.732	36.6
BL+	DF-3	1.6210	2.762	36.2
BL+	EDF-1	1.6490	2.959	33.8
Pitt	EDF-2	1.6725	3.106	32.2
BL	EDF-2	1.6890	3.236	30.9
Pitt	VDF-1	1.7000	3.300	30.3
BL+	EDF-3	1.7200	3.413	29.3

* BL, Bausch & Lomb Optical Co.; BL+, Bausch & Lomb catalogue values (also manufactured by other firms such as Pittsburgh Plate, Libbey-Owens-Ford, and Hayward); Pitt, Pittsburgh Plate Glass Co.; Corn, Corning Glass Works; and EK, Eastman Kodak Co.

These glasses are shown diagrammatically on Fig. 1, connecting refractive index and dispersive power.

obtained by using weak elements differing widely in dispersive powers or by using stronger elements, which are closer in dispersive powers. If weak elements are desired for some reason, as is particularly the case in telescope and microscope objectives, glasses should be chosen which have the greatest possible difference in dispersive powers, such as a dense flint and a light borosilicate crown. In many types of photographic objective, however, rather strong elements are often needed, and in such cases glass types that do not differ too widely in dispersive power may deliberately be chosen. It is often possible to ignore achromatism completely for a great part of the design time and to consider it only toward the end when it is necessary to decide definitely which actual glass types will be used.

If the problem of achromatizing a lens is analyzed in detail, the contribution of any element to the total chromatic aberration will be proportional to the dispersion of the glass and also to the difference between the lengths of the extreme outer and central rays within the element[1] (Fig. 2). That is, the contribution of a lens element to the final chromatic aberration between the G′ and D spectral lines is proportional to the product of $(D-d)$ and $(n_{G'}-n_D)$ for that element. This relation can be shown to reduce to the approximate rule that the chromatic aberration contribution of an element is proportional to

$$y^2w/f$$

f = focal length of the particular element being considered.
w = dispersive power of glass over wave-length range.
y = height of incidence of extreme marginal ray at that element.

III. Lateral Color Correction

There is a second kind of chromatic aberration which must be carefully eliminated in many types of lens, namely, "lateral color" or "chromatic difference of magnification." It is essentially a chromatic variation in the size of the image in contrast to ordinary chromatic aberration, which is a chromatic variation in the position of the image.

To correct lateral color, the use of positive elements of low dispersion in combination with negative elements of high dispersion is unnecessary because the whole problem is now one of securing a proper balance between the elements ahead of the stop and those behind the stop. A positive element ahead of the stop acts in the same way as a negative element behind the stop, the contribution of each element to the total lateral color being proportional to the power of the element, the dispersive power of the glass, and the distance of the element from the stop. The lower diagram in Fig. 3 indicates schematically how the various elements act in respect to lateral color, that is, as if they were forces acting on a lever with the fulcrum of the lever at the diaphragm position. A positive element in the front member tends to cause the blue image to be above the red, as indicated by an anticlockwise rotation of the lever, and so does a negative element in the rear member. A negative element, however, in front or a positive element behind tends to form a blue image which is smaller than the red image, corresponding to a clockwise rotation of the lever.

It is therefore quite possible to select the powers, positions, and dispersive powers of all the elements in a lens so that the total of the contributions of all the elements to the longitudinal as well as the lateral color separately add up to zero.

IV. Factors Determining Choice of Refractive Index

The conditions which determine the exact choice of

[1] R. Glazebrook, Dictionary of Applied Physics, Vol. IV, article by A. E. Conrady on "Microscope, Optics," p. 225. Macmillan Company, London, 1923. 914 pp.

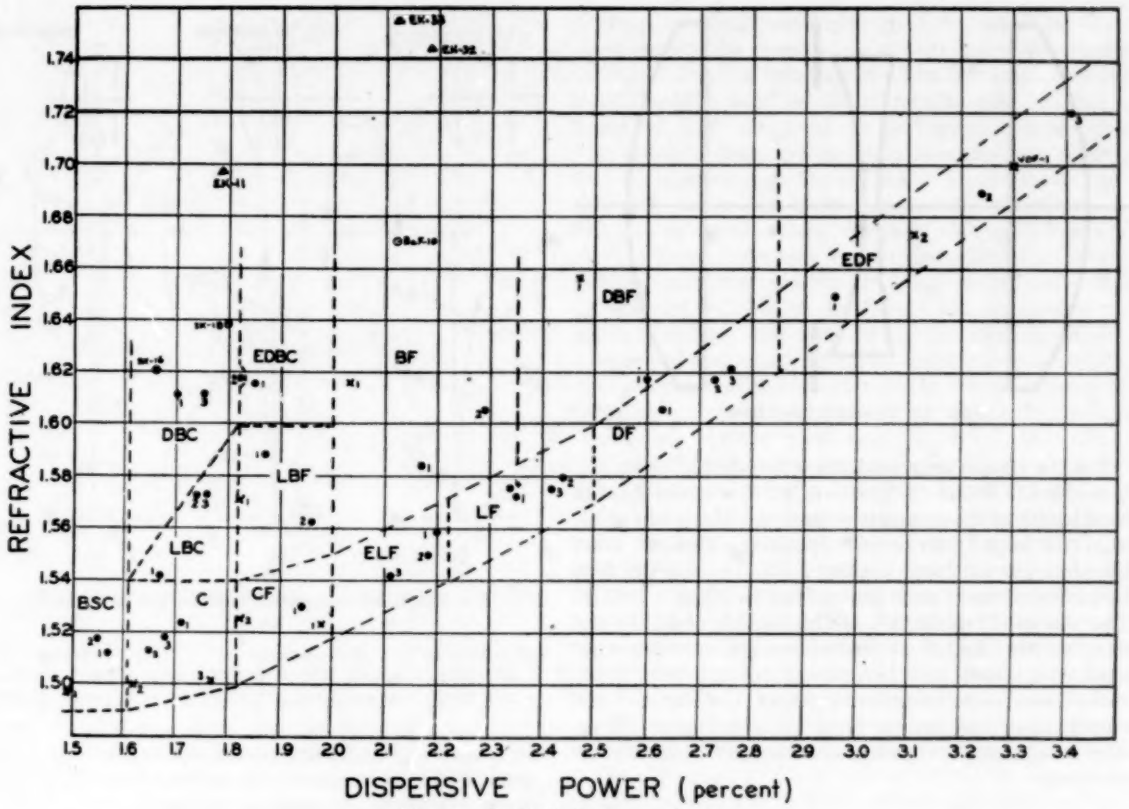

FIG. 1.—Optical glass-type chart.

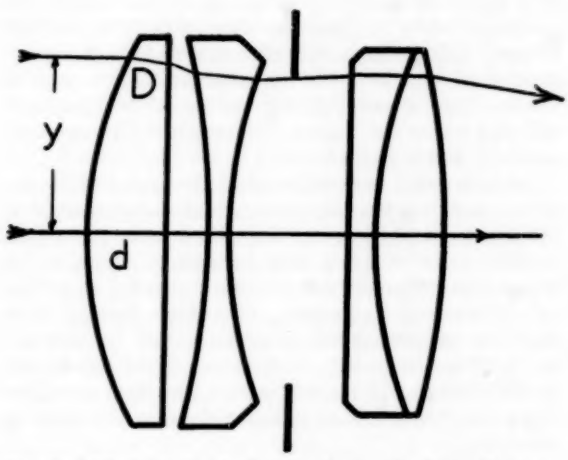

FIG. 2.—Method of calculating chromatic aberration contributions of separate elements in lens.

refractive indices for the various elements in a lens are not nearly so easily discussed as were those governing the choice of dispersive powers. Indeed, in types of lens, such as the Cooke Triplet (Fig. 4), in which no cemented surfaces are employed, a good lens may be designed using almost any desired selection of refractive indices whatever. In other cases and particularly when cemented surfaces are used, the relation between the various refractive indices is quite an important

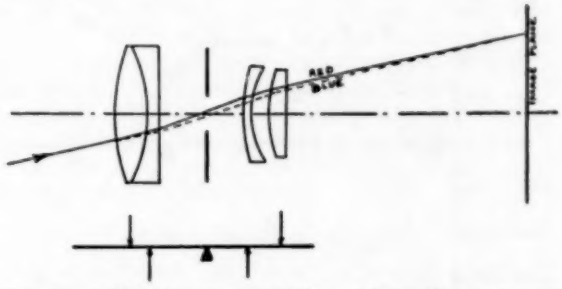

FIG. 3.—Schematic representation of balancing of lateral color between two halves of lens system.

feature of the design. A few examples will suffice to show how significant may be the selection of refractive indices in some particular cases.

V. Design of Telescope Objective

In a simple cemented telescope objective, the positive element is made of crown glass and the negative element of flint glass and the dispersive powers are generally widely spaced. A common selection is a crown (*a*) with (approx.) $n = 1.517$, $w = 1.550\%$ and a flint (*b*) with $n = 1.617$, $w = 2.732\%$. The focal lengths of the two components are determined so as to achromatize the lens as shown by formulas (1) and (2).

$$f_a = F\left(\frac{w_b - w_a}{w_b}\right) \quad (1)$$

$$f_b = F\left(\frac{w_a - w_b}{w_a}\right) \quad (2)$$

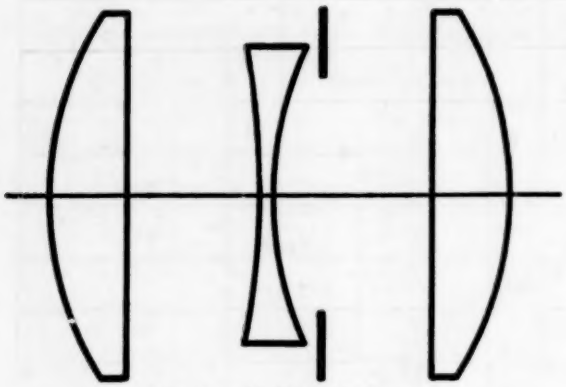

FIG. 4.—Cooke triplet lens.

For the glasses suggested, these formulas give for (1), $f_a = +0.433\ F$ and (2) $f_b = -0.762\ F$, wherein F is the focal length of the complete objective. For a lens of 10-in. focal length, the crown (positive) element must therefore have a focal length of 4.33 in. and the flint (negative) element must have a focal length of −7.62 in. The shapes ("bendings") of the two elements do not significantly affect the achromatism but only the other aberrations, such as spherical and coma. Even if the two elements are cemented together, the shape of the combination may still be regarded as a degree of freedom which may be varied in order to correct some other aberration.

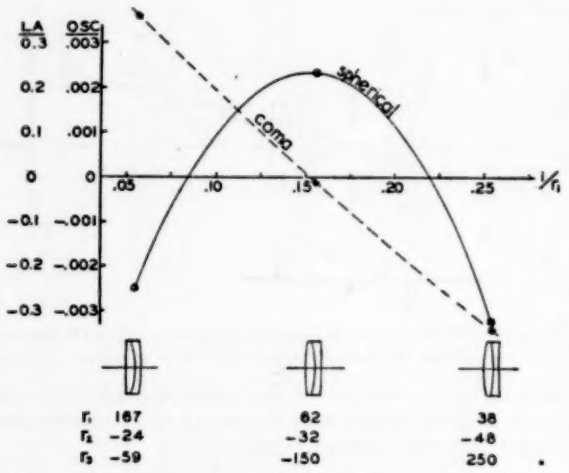

FIG. 5.—"Bending" a lens; its effect on spherical aberration and coma.

If several different "bendings" are used and the shape of the lens in each case is defined by the curvature $1/r$ of its first surface and if computations are made for the spherical aberration and coma of each, a graph may be plotted connecting these two aberrations with the lens shape (see Fig. 5). This graph will show at once what shape the lens must have in order to be either spherically corrected or coma corrected.

It will be clear that this process can be carried through with any arbitrary choice of glass types except that the dispersive-power difference ($w_a - w_b$) must be as large as possible in order to make the surface curvatures of the lens as weak as possible.

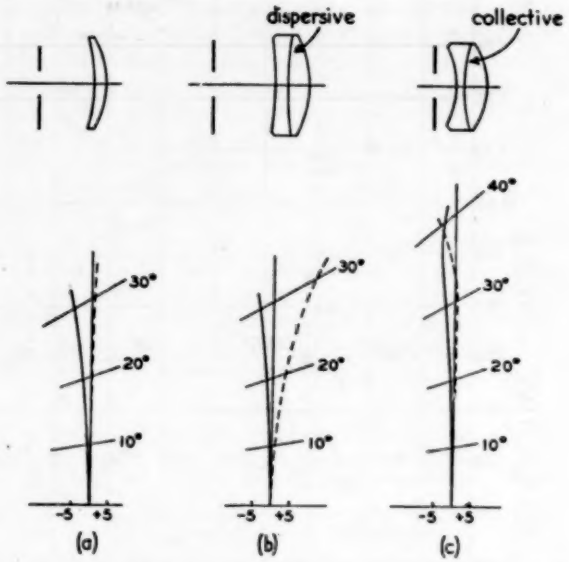

FIG. 6.—Effect of cemented surface on astigmatism of lens.

(a) Wollaston	(b) Chevalier		(c) Schröder	
$n = 1.523$	$n = 1.617$	1.512	$n = 1.550$	1.611
$w = 1.71\%$	$w = 2.76\%$	1.65%	$w = 2.18\%$	1.70%

As far as the choice of refractive indices is concerned, it is found that for any given dispersion values, the parabolic curve of spherical aberration in Fig. 5 will rise and fall as the index difference ($n_b - n_a$) is made greater or smaller. If, for example ($n_b - n_a$) is smaller than about 0.04, the vertex of the parabola will sink below the x axis, and no spherically corrected solutions will be possible.

An interesting case arises when the vertex of the parabola just touches the x axis, which occurs usually at the point where the coma line also crosses the x axis. At that value of $1/r$, a lens is obtained which is corrected simultaneously for chromatic aberration, spherical aberration, and coma. Objectives having these desirable properties are generally called "aplanatic," and they are frequently used, especially for fire-control instruments in which the objective lens must give good definition over a field as wide as 5 degrees or more from the axis.

As this is an interesting case in which the precise selection of glass types is an essential part of the design procedure, it may be of interest to discuss it in some detail. A suitable flint glass is selected arbitrarily, for example, EDF–2, which has an index of 1.689 and a dispersive power of 3.106%. An arbitrary refractive index of 1.517, for example, is chosen for the crown glass, and the two available degrees of freedom, namely (r_2/r_1) and (r_3/r_1), being used to correct spherical aberration and coma. The dispersive power that the crown glass must have in order to achromatize the system is then determined, and a point may be

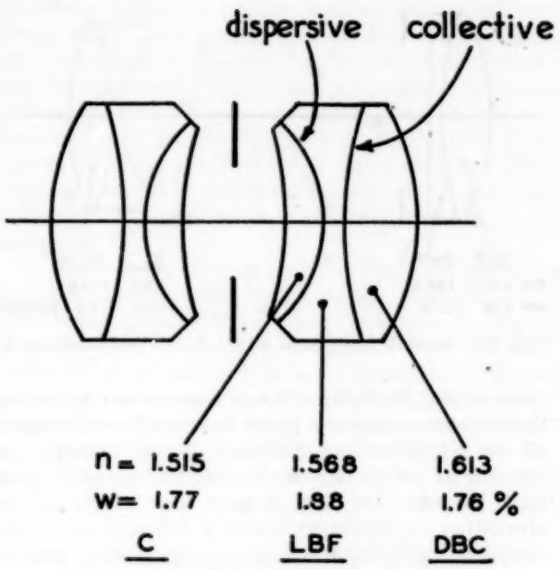

FIG. 7.—Goerz "Dagor" lens (see footnote 2).

marked on the glass chart, Fig. 1, to represent one possible crown glass to go with this particular flint glass to form an aplanat. The design is repeated using a crown index of 1.5725, and the desired value of w for this crown is again determined, and so on. In this way, a series of points may be plotted to form a curve, which is actually almost a straight line on the glass chart, representing the locus of all possible crown glasses to go with the chosen flint glass, EDF–2, to make aplanatic lenses. If this line passes through some available glass, that will be the glass to use. If no crowns are available, a new type of flint must be selected and the process repeated.

VI. Collective and Dispersive Cemented Surfaces

In the doublet telescope objectives just described, the cemented surface acts like the surface of a concave lens because the refractive index of the flint glass is higher than that of the crown glass. Such a surface has the property of spreading out the rays of a parallel beam incident upon it, and therefore it is commonly said to be a "dispersive" surface although no question of color dispersion is involved.*

Not all cemented surfaces, however, are dispersive. In some types of photographic objective, the refractive index of the crown component is deliberately chosen to be higher than that of the flint component, thus giving the cemented surface the properties of a convex lens surface. Such a surface is called "collective," and it acts in the opposite way to the dispersive surface in a telescope objective. A collective surface leads to undercorrection of spherical aberration and therefore cannot be used as a means for correcting that aberration. The real use of a collective cemented surface, however, appears in lenses which normally have over-corrected astigmatism in the outer parts of the field; for instance, the three lenses shown diagrammatically in Fig. 6 may be considered. The left-hand lens (a) is of the type used in cheap box cameras. It has a fairly flat field† out to about 20 degrees from the axis with enough spherical aberration to compel the restriction of its aperture to about f/14. It also shows considerable chromatic aberration and lateral color. If this lens is achromatized by use of the "old" types of glass, namely, common crown and flint, the achromatized landscape lens is obtained, which was introduced by C. Chevalier in 1821. The dispersive cemented surface now acts in an increasingly strong manner on the oblique pencils, resulting in a serious overcorrection of the astigmatism in the outer parts of the field, accompanied, however, by improved spherical aberration. In the third case, Fig. 6 (c), the refractive index of the crown glass is higher than that of the flint glass, producing a collective cemented surface, which has the effect of introducing an increasing undercorrection of the astigmatism in the outer parts of the field to such an extent that the tangential field at 40 degrees actually turns around and comes within the sagittal field. This lens has somewhat increased spherical aberration, but its excellent field characteristics have earned for it the name of "anastigmat landscape lens." Inasmuch as this lens employs the "new" glass types (barium crown) introduced by Abbe and Schott in 1888, it is often referred to as a "new achromat."

The advantages of a dispersive surface in correcting spherical aberration, and of a collective surface in eliminating astigmatism, are combined in lenses of the Goerz "Dagor" type, designed by von Höegh[2] and Goerz in 1893 (see Fig. 7). In lenses of this type, the choice of glasses is fundamental to the whole success of the design, both in respect to dispersive powers and refractive indices. It is a sensitive lens to manufacture, and if the glass constants change from one melt to another, it is necessary to recompute the lens radii to compensate for these changes.

VII. Petzval Condition

It can be shown that if a lens is to have a flat field and be free from astigmatism, there is a fundamental condition which must be satisfied, named after the Austrian mathematician, Petzval (equation (3)).

$$\sum \frac{1}{nf} = 0 \qquad (3)$$

n = refractive index of element in lens.
f = its thin-lens focal length given by

$$\frac{1}{f} = (n - 1)\left(\frac{1}{r_1} - \frac{1}{r_2}\right).$$

It is generally unnecessary to bring this sum absolutely to zero, but it must be drastically reduced if a satisfactory anastigmatic flattening of the field of the lens is to be achieved.

* It might be better to coin a new adjective here, such as "divergent," but the word "dispersive" is thoroughly intrenched both in the literature and in common usage.

† The field curves shown beneath the lens diagrams represent the loci of the images of tangential lines (dotted) and radial lines (solid).

[2] E. von Höegh, and C. P. Goerz, "Lens for Optical Purposes," U. S. Patent 528,155, Oct. 30, 1894.

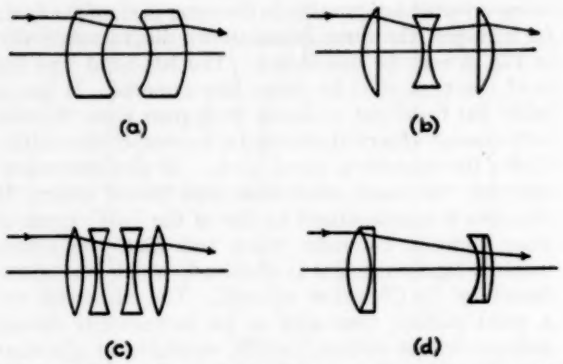

FIG. 8.—Means for reducing Petzval sum of photographic objectives.

If formula (3) is studied, the condition will be found to be most readily satisfied if the positive elements have a high refractive index and the negative elements a low index and also if the total power of the negative elements is almost equal to the total power of the positive elements. The conditions embodied in equation (3) for a flat field are therefore exactly opposite those just outlined for a telescope objective, and, as a result, no cemented telescope objective can possibly have a flat anastigmatic field.

VIII. Design of Anastigmat Lenses

The only way to achieve a spherically corrected achromatic objective, which also satisfies the Petzval condition, is to strengthen the negative components and space the elements apart so that the beam of light passing through the lens will have a smaller diameter at the negative elements than at the positive elements. A few typical systems in which this has been done are indicated in Fig. 8. In these, and indeed in all modern photographic objectives, the positive elements are made chiefly of high-index, low-dispersion glass, such as the dense barium crowns; the negative elements are of flint glass, having higher dispersion and any suitable refractive index. The precise choice of glasses is often a matter of considerable difficulty to the designer be-

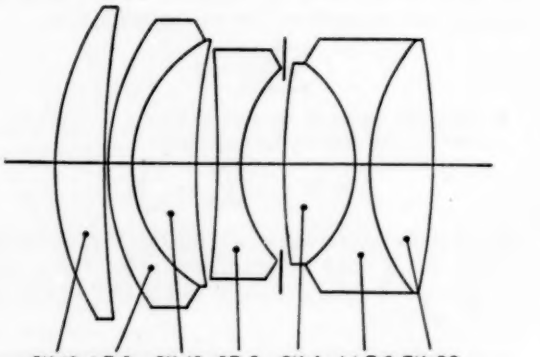

FIG. 9.—Kodak "Ektar" f/1.5 (see footnote 3).

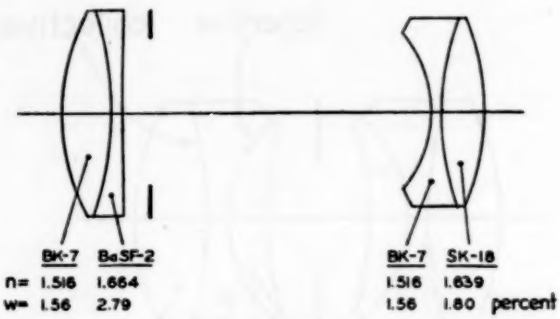

FIG. 10.—Kodak Telephoto Ektar f/3.8 (see footnote 4).

cause raising the index of a lens element and weakening the surfaces to maintain power has the effect of reducing all the aberration contributions of that element; increasing an air space so as to alter the diameter of the light beam at the lens element also affects all the aberration contributions but in a different way. The designer has thus at his disposal the following series of variables (degrees of freedom) with which, by suitable manipulation, all the aberrations of the lens must be corrected: (1) the radii of all the surfaces, (2) air spaces, (3) refractive indices and the dispersive powers of the glasses, and sometimes also (4) thicknesses of the elements. It is not surprising that the complete design of an elaborate modern anastigmat lens may take a year or more, most of that time being used to make innumerable systematic trials and errors with occasional simultaneous solutions aimed at correcting several faults in the lens at the same time. The final result is a delicate and somewhat unstable balance between many opposing tendencies, and a very slight derangement of the lens or of the properties of the glasses used in it may throw the corrections off so badly as to render the lens useless.

As an example of the use of a variety of glass types in a modern anastigmat lens, Fig. 9 shows a diagram of the Kodak Ektar f/1.5 lens, designed by Schade,[3] together with the glass types taken from the Schott catalogue. It will be noticed that there are seven elements, of which four are positive and three are negative, and that the refractive indices of the positive elements are all very high, namely, 1.64, 1.64, 1.61, and 1.74. The refractive indices of the negative elements are, respectively, 1.57, 1.67, and 1.53. All three cemented surfaces are collective, their chief function being to smooth out the zonal residuals of axial and oblique spherical aberration.

Figure 10 shows a typical modern telephoto lens, patented by Bennett[4] in 1941. The front member resembles a telescope objective, being made of a light borosilicate crown and a heavy barium flint. It is an achromat with a dispersive cemented surface. The rear member is an achromatic negative system, comprising a strong negative element of borosilicate crown

[3] W. Schade, "Photographic Objective," U. S. Patent 2,259,004, Oct. 14, 1941.
[4] H. F. Bennett, "Telephoto Objective," U. S. Patent 2,231,699, Feb. 11, 1941.

glass cemented to a weaker positive element of very dense barium crown glass. In most telephoto lenses, the rear negative member bends the oblique beams upward too much, leading to pincushion distortion, but the strong collective cemented surface in the rear member in the present design serves to bend the beam downward, thus correcting the distortion very effectively. The design shown in Fig. 10 covers a half field of about 9 degrees with excellent correction of all aberrations.

The lens designer owes a great debt of gratitude to the glass manufacturer for the variety of his products and for the remarkable constancy of optical properties which he is able to achieve. It may be hard to write a formal definition of "optical glass," but everyone knows what that word means in actual practice. The development of lenses and that of optical glass have gone hand in hand, and with each advance in glass has come a corresponding advance in lens design The modern era in photographic lenses dates from the introduction of barium crown glasses by Schott in 1888, and although no limit has been reached as to what can be done in the use of those glasses, any new types, which are in some way more extreme than anything now available, will be welcomed.

The various types of glass are the designer's tools. Give him a better tool and, after he has learned how to use it, better products may be expected from his workshop. With the present-day development of some entirely new kinds of optical glass, there may be almost a revolution in lens design during the coming decade, but as no tool works by itself, a new and better lens must ever remain a monument to the patience, skill, and tireless energy of the lens designer

SCIENTIFIC DEPARTMENT, HAWK-EYE WORKS
EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK

Ceramic Frontiers
Still Ahead of Us

Recent Tempo in Proving Uses of Available Minerals

√ *New Compositions*
√ *More Economical and More Positive Processing*
√ *More Certain Product and Process Controls*

Resulting in Improved Products at Lower Costs Show That

Ceramic Frontiers

Have Yet to Be Reached and Can Be Approached Only by Constant

Research Vigilance

353

[*THREE HUNDRED AND FIFTY-THREE CORPORATIONS*]

ON MAY 1, 1944

Have Paid a Minimum Sustaining Fee of Twenty-Five Dollars ($25.00)

[*Some* of These Have Paid *More* Than This Minimum]

Another Twelve (12) Corporations Have Asked to Be Billed

Making a TOTAL of

365

[*THREE HUNDRED AND SIXTY-FIVE CORPORATIONS*]

Giving Financial and Moral Support

That Personal Members of

The American Ceramic Society, Incorporated

May Share the Benefits of Cooperation at the

Low Annual Cost of Twelve Dollars and Fifty Cents ($12.50)

OFFICIAL PERSONNEL OF DIVISIONS, 1944–1945

	Design	Enamel	Glass	Materials and Equipment	Refractories	Structural Clay Products	White Wares
Trustee	W. A. Weldon	R. L. Fellows	J. S. Gregorius	J. E. Eagle	J. B. Austin	Frederick Heath, Jr.	J. W. Hepplewhite
Chairman	W. A. Weldon	H. D. Carter	K. C. Lyon	J. R. Kauffman	W. R. Kerr	R. L. Stone	J. W. Whittemore
Vice-Chairman	Theodore Lenchner	W. W. Higgins	Louis Navias	J. F. Day	S. M. Swain	E. F. Theobald	R. M. Campbell
Secretary	Myrtle M. French	D. G. Moore	S. R. Scholes	V. J. Roehm	E. E. Callinan	V. W. Boeker	C. M. Lambe, Jr.
Division Nominations	Alice A. Ayars K. E. Smith	F. R. Porter M. J. Bahnsen Karl Kautz	R. A. Miller W. R. Lester L. W. Peterson	J. F. McMahon E. M. Rupp	J. B. Austin C. L. Thompson G. J. Easter	A. P. Potts R. L. Ferguson C. F. Wiseman	J. R. Beam F. C. Henderson R. Russell, Jr.
Papers and Program	C. M. Harder Vincent Brocmhall H. L. Moody	W. W. Higgins	Louis Navias	W. E. Dougherty E. W. Emrich J. S. Breitenstein	E. B. Read C. A. Freeman W. S. Debenham B. L. Dorsey	A. C. Jackson H. L. Winburn J. G. Seanor	E. P. McNamara
Membership	W. J. Harr Herbert Tepping G. W. Fichter C. K. Williams	A. I. Andrews J. F. Hunt F. A. Petersen	F. V. Tooley R. R. Shively	V. V. Kelsey	L. C. Hewitt F. E. Lobaugh H. M. Parkhurst E. M. Sarraf	C. F. Tefft R. R. Robinson	A. A. Wells
Standards		R. L. Cook W. N. Harrison R. M. King F. A. Petersen B. W. King, Jr.	Members are Comm. C-14, A.S.T.M.	R. C. Meeker		G. R. Robinson	F. P. Hall L. E. Thiess
Research		J. C. Reimers	Alexander Silverman O. G. Burch C. E. Leberknight	R. R. Robinson	E. C. Petrie	G. A. Bole H. C. Plummer	R. Russell, Jr. Glenn Howatt
Classification and Nomenclature	Mrs. J. W. Dixon	G. H. McIntyre E. E. Bryant	E. P. McNamara	J. F. McMahon	C. M. Dodd	E. F. Theobald R. E. Grim	A. S. Watts
Rules	J. P. Thorley	W. A. Deringer O. E. Mulvane	S. R. Scholes	Philip Dressler	S. F. Walton	Howells Fréchette	J. D. Clark
Councillors		D. G. Bennett	R. W. Wampler J. F. Greene	V. V. Kelsey		L. R. Whitaker A. P. Potts	
Exhibitions	Mrs. L. S. Backus		J. E. Frazier				
Industrial Management			C. J. Uhrmann	S. S. Cole	J. L. Crawford	J. C. Peck	
Bibliography	P. E. Cox	J. E. Rosenberg		C. L. Cruikshank			

Officers of Classes

	Institute of Ceramic Engineers	Ceramic Educational Council
Trustee	H. M. Kraner	R. M. Campbell
President	M. F. Beecher	C. M. Dodd
Vice-President	T. A. Klinefelter	A. I. Andrews
Secretary	R. S. Bradley	P. S. Dear

THE AMERICAN CERAMIC SOCIETY TRUSTEES AND OFFICERS FOR 1944–1945

President: E. H. Fritz, Stupakoff Ceramic & Mfg. Co., Latrobe, Pa.
Vice-President: C. Forrest Tefft, The Claycraft Co., Columbus, Ohio
Treasurer: J. D. Sullivan, Battelle Memorial Institute, Columbus 1, Ohio
Secretary-Editor: R. C. Purdy, 2525 North High St., Columbus 2, Ohio
Past-President: C. E. Bales, Ironton Fire Brick Co., Ironton, Ohio
Past-President: L. J. Trostel, General Refractories Co., Baltimore, Md.

TRUSTEES FROM INDUSTRIAL DIVISIONS*

Design: W. A. Weldon, Locke Insulator Corp., Baltimore, Md. (1946)
Enamel: R. L. Fellows, Chicago Vitreous Enamel Product Co., Cicero, Ill. (1946)
Glass: J. S. Gregorius, Pittsburgh Plate Glass Co., Pittsburgh, Pa. (1947)
Materials and Equipment: J. E. Eagle, 6306 20th Ave., Green Meadows, Hyattsville, Md. (1945)
Refractories: J. B. Austin, U. S. Steel Corp., Kearny, N. J. (1946)
Structural Clay Products: Frederick Heath, Jr., Owens-Corning Fiberglas Corp., Toledo, Ohio (1945)
White Wares: J. W. Hepplewhite, Edwin M. Knowles China Co., Newell, W. Va. (1947)
nstitute of Ceramic Engineers: H. M. Kraner, Bethlehem Steel Co., Bethlehem, Pa. (1947)
Ceramic Educational Council: R. M. Campbell, New York State College of Ceramics, Alfred, N. Y. (1947)

* Date of expiration of term of office in parentheses.

DIVISION OFFICERS

Design
Chairman: W. A. Weldon, Locke Insulator Corp., Baltimore, Md.
Secretary: Myrtle M. French, Art Institute of Chicago, Chicago, Ill.

Enamel
Chairman: H. D. Carter, Harshaw Chemical Co., Cleveland, Ohio
Secretary: D. G. Moore, National Bureau of Standards, Washington, D. C.

Glass
Chairman: K. C. Lyon, Armstrong Cork Co., Millville, N. J.
Secretary: S. R. Scholes, N. Y. State College of Ceramics, Alfred, N. Y.

Materials and Equipment
Chairman: J. R. Kauffman, Allied Engineering Co., Millville, N. J.
Secretary: V. J. Roehm, Kentucky Clay Mining Co., Alliance, Ohio

Refractories
Chairman: W. R. Kerr, Armstrong Cork Co., Beaver Falls, Pa.
Secretary: E. E. Callinan, Timken Roller Bearing Co., Timken Steel & Tube Div., Canton, Ohio

Structural Clay Products
Chairman: R. L. Stone, Univ. of North Carolina, Raleigh Unit, Raleigh, N. C.
Secretary: V. W. Boeker, Owens-Corning Fiberglas Corp., Toledo, Ohio

White Wares
Chairman: J. W. Whittemore, Virginia Polytechnic Institute, Blacksburg, Va.
Secretary: C. M. Lambe, Jr., Univ. of North Carolina, Raleigh Unit, Raleigh, N. C.

OFFICERS OF THE FELLOWS

Dean: R. B. Sosman, U. S. Steel Corp., Kearny, N. J.
Associate Dean: Howells Fréchette, Bureau of Mines, Ottawa, Ontario, Canada.
Secretary-Treasurer: R. M. King, Ohio State University, Columbus, Ohio

INSTITUTE OF CERAMIC ENGINEERS

President: M. F. Beecher, Norton Company, Worcester, Mass.
Vice-President: T. A. Klinefelter, U. S. Bureau of Mines, Tuscaloosa, Ala.
Secretary: R. S. Bradley, A. P. Green Fire Brick Co., Mexico, Mo.

CERAMIC EDUCATIONAL COUNCIL

President: C. M. Dodd, Iowa State College, Ames, Iowa
Vice-President: A. I. Andrews, University of Illinois, Urbana, Ill.
Secretary: Paul S. Dear, Virginia Polytechnic Institute, Blacksburg, Va.

LOCAL SECTIONS

Baltimore-Washington
Chairman: W. R. Lester, Maryland Glass Co., Baltimore, Md.
Secretary: J. H. Veale, General Refractories Co., Baltimore, Md.

Central Ohio
Chairman: H. J. Orlowski, O.S.U. Engr. Expt. Sta., Columbus, Ohio
Secretary: A. C. Jackson, Claycraft Co., Columbus, Ohio

Chicago
Chairman: Hugo Filippi, 228 N. LaSalle St., Chicago, Ill.
Secretary: J. J. Svec, Industrial Publications, Inc., 59 E. Van Buren St., Chicago, Ill.

Michigan-Northwestern Ohio
Chairman: J. F. Quirk, A C Spark Plug Co., Flint, Mich.
Secretary: W. V. Blake, Macklin Co., Jackson, Mich.

Northern California
President: W. V. Bragdon, California Faience Co., Berkeley, Calif.
Secretary: P. C. Valentine, Del Monte Properties Co., San Francisco, Calif.

Pacific-Northwest
President: Howard Mansur, Washington Brick & Lime Co., Spokane, Wash.
Secretary: J. A. Pask, Univ. of Washington, Seattle, Wash.

Pittsburgh
Chairman: W. C. Rueckel, Koppers Co., Pittsburgh, Pa.
Secretary: J. W. Jordan, Mellon Institute, Pittsburgh, Pa.

Southern California
Chairman: R. H. Evans, Gladding McBean, & Co. Glendale, Calif.
Secretary: Guy Wurtsbaugh, Pacific Clay Products Co., Los Angeles, Calif.

St. Louis
Chairman: H. H. Hanna, Pittsburgh Plate Glass Co., Crystal City, Mo.
Secretary: J. H. Ivery, Hydraulic Press Brick Co., St. Louis, Mo.

Upstate New York
Chairman: M. H. Berns, Electro Refractories & Alloys Corp., Buffalo, N. Y.
Secretary: E. E. Kunzman, Titanium Alloy Mfg. Co., Niagara Falls, N. Y.